THE FREE ENERGY OF THE NORMAL ALIPHATIC ALCOHOLS IN AQUEOUS SOLUTION.

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Thesis for the Degree of Doctor of Philosophy.

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Part I (A).

The partial vapour pressures of binary solutions of methyl alcohol in water.

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INTRODUCTION.

The partial vapour pressures of ethyl alcohol-water mixtures have been determined recently at 25°C by Dobson (J. Chem. Soc., 127, 2871, 1925), Shaw and Butler (Proc. Roy. Soc., 129A, 519, 1930) and Thomson (Thesis, Edinburgh University, 1932). The vapour pressure curve of ethyl alcohol is given in Fig. I and the experimental data in Table I. This curve is typical of the vapour pressure curves of the aliphatic alcohols in aqueous solution.

Table I./

Fig. 1.

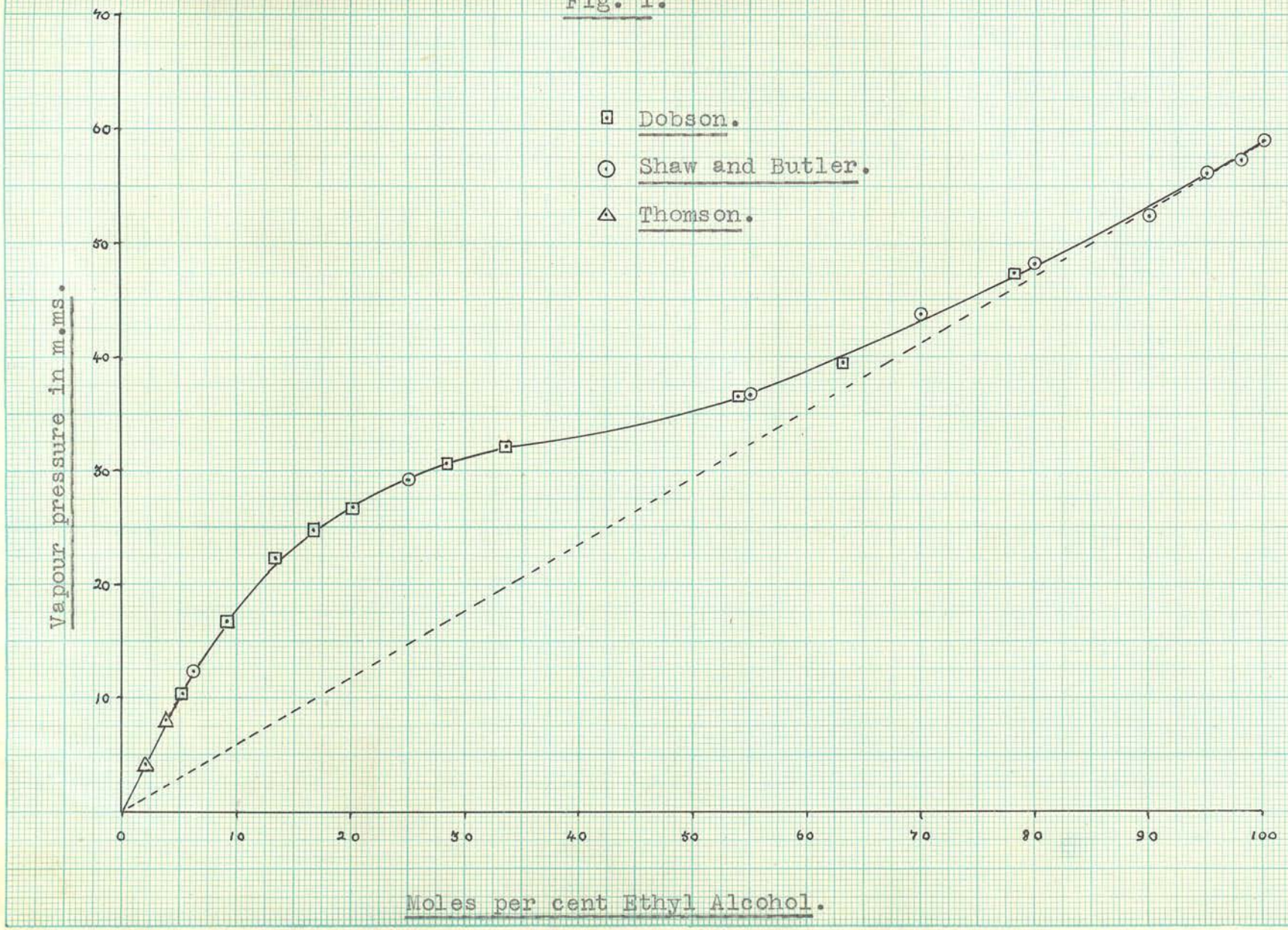

Dobson.
Shaw and Butler.
Thomson.
Vapour pressure in m.ms.
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
Moles per cent Ethyl Alcohol.

TABLE I.

N_a	p_a Shaw and Butler.	p_a Dobson.	p_a Thomson.
2·00			4·08
4·00			8·16
5·23		10·50	
6·40	12·29		12·32
9·17		16·66	
13·44		22·27	
16·71		24·90	
20·22		26·85	
25·00	29·08		
28·49		30·73	
33·69		32·16	
49·04		36·64	
50·00	36·65		
58·21		39·53	
70·00	43·62		
78·14		47·40	
80·00	48·04		
90·00	52·42		
95·00	56·03		
98·00	57·24		
100·00	58·98	59·01	

N_a = Moles per cent of alcohol in solution.

p_a = Partial vapour pressure of alcohol in m.m. of mercury.

In dilute solutions, it will be seen that the curve is linear and the partial vapour pressure of the alcohol very nearly proportional to the mole fraction of alcohol in the solution. If the mixtures obeyed Raoult's Law the partial vapour pressure would be exactly proportional to the mole fraction and the relationship would be represented by the dotted straight line. Thus the partial vapour pressure of ethyl alcohol in aqueous solution is greater than that required by Raoult's Law, but corresponds to it in very dilute solutions. If the linear portion of the curve be extrapolated to the axis of 100% alcohol, the vapour pressure of the pure alcohol, as given by the intercept on the axis, that is, if it existed under the conditions of dilute aqueous solutions, is greater than that of the pure alcohol under normal conditions.

It can be shown thermodynamically that the partial molal free energy of a binary mixture of volatile, mutually soluble liquids whose vapours obey the ideal gas laws is given by,

$$F = F^{o} + RT \log p/p^{o} \quad \ldots\ldots\ldots\ldots (1)$$

where F is the partial molal free energy of the solute in solution.

F^{o} is the molal free energy of the pure liquid solute.

p is the partial vapour pressure of the solute over the solution.

p^{o} is the vapour pressure of the pure liquid solute, all at the same temperature.

Thus, in a binary solution of alcohol in water, we have two equations,

$$F_a = F_a^{\circ} + RT \log p_a/p_a^{\circ} \quad \ldots\ldots\ldots\ldots(2)$$

$$F_w = F_w^{\circ} + RT \log p_w/p_w^{\circ} \quad \ldots\ldots\ldots\ldots(3)$$

where F_a and F_w are the partial molal free energies of alcohol and water.

F_a° and F_w° are the molal free energies of pure alcohol and water.

p_a and p_w are the partial vapour pressures of alcohol and water.

p_a° and p_w° are the vapour pressures of pure alcohol and water, all at the same temperature and when the alcohol and water vapours can be regarded as perfect gases.

As we have seen, when a solution obeys Raoult's Law the partial vapour pressure of each component is proportional to its mole fraction in solution, therefore,

$$p_a/p_a^{\circ} = N_a \quad \text{and} \quad p_w/p_w^{\circ} = N_w$$

where N_a is the mole fraction of alcohol in solution.

N_w is the mole fraction of water in solution.

Hence in a very dilute solution of the alcohol, in which Raoult's Law holds, its partial molal free energy is given by,

$$F_a = F_a^{\circ'} + RT \log N_a \quad \ldots\ldots\ldots\ldots(4)$$

where $F_a^{\circ'}$ is the molal free energy of the pure alcohol under the conditions of infinite dilution,

that is, if the alcohol molecules are not appreciably associated.

Combining equations (2) and (4) we have therefore,

$$F_a^{o'} - F_a^{o} = RT \log p_a / p_a^{o} x N_a \quad \ldots\ldots\ldots(5)$$

The activity coefficient of the alcohol is defined as

$$f_a = p_a / p_a^{o} x N_a$$

hence if f_a^{o} is the activity coefficient of the alcohol at the dilution for which (4) holds, we have

$$F_a^{o'} - F_a^{o} = RT \log f_a^{o} \quad \ldots\ldots\ldots(6)$$

the value of f_a^{o} can be determined by extrapolation of the values of the activity coefficient in dilute solutions, to zero concentration and its value corresponds to the apparent value of the vapour pressure of the pure alcohol under the conditions of very dilute solutions mentioned previously. Knowing the value of f_a^{o} the value of $(F_a^{o'} - F_a^{o})$ can be calculated and represents the difference between the molal free energy of the alcohol in very dilute solution and the molal free energy of the pure alcohol. It can be regarded as the difference in free energy of a molecule of alcohol surrounded entirely by water molecules and that of the molecule surrounded entirely by alcohol molecules.

The necessary data for calculating this free energy difference have been determined for ethyl alcohol, as previously mentioned, and, more recently, Thomson (loc. cit.) has studied the systems of n-propyl and n-butyl alcohols in water at 25°C.

Previous to Thomson's work, the only extensive measurements made with alcohols other than ethyl, were those of Vrewski (Z. phys. Chem., 81, 1, 1912) for methyl and propyl alcohols at various temperatures above 30°C and those of Ferguson and Funnell (J. Phys. Chem., 33, 1, 1929) at 39·9°C, for methyl alcohol.

From the very limited data then existing, Butler (Proc. Roy. Soc., 135A, 364, 1932) postulated that each additional carbon atom in the chain of an aliphatic alcohol should increase the free energy difference by a constant amount. The data on which this conclusion was based are given below:-

	Temp.	p_a/N_a	p_a^o	f_a^o	$F_a^{o'} - F_a^o$	Δ
Methyl alcohol	40°C	445	261	1·7	314 cals.	
Ethyl alcohol	25°C	180	59	3·0	651 cals.	337
Propyl alcohol	30·3°C	200	28·5	7·0	1183 cals.	532

Thomson (loc. cit.) repeated some ethyl alcohol determinations at low concentrations and his work on the partial vapour pressures of n-propyl and n-butyl alcohols in aqueous solution further confirmed the hypothesis. These results are given below:-

	Temp.	p_a/N_a	p_a^o	f_a^o	$F_a^{o'} - F_a^o$	Δ
Ethyl alcohol	25°C	218	58·98	3·70	775 cals.	
N-propyl alcohol	25°C	283	27·76	13·01	1519 cals.	744
N-butyl alcohol	25°C	350	6·96	50·29	2320 cals.	801

In order to complete the series, it was decided to determine the partial vapour pressures of methyl alcohol in aqueous solutions at 25°C and so calculate the value of $(F_a^{o'} - F_a^{o})$.

EXPERIMENTAL.

I. Method of Experiment.

The air bubbling method was used for determining the partial vapour pressures of the methyl alcohol-water mixtures. This method has been extensively used by Perman (Proc. Roy. Soc. A., 72, 72, 1903); (Trans. Faraday Soc., 23, 95, 1927) for aqueous solutions and by Foote and Scholes (J. Amer. Chem. Soc., 33, 1317, 1911), Dobson (J. Chem. Soc., 127, 2871, 1925), Shaw and Butler (Proc. Roy. Soc. A., 129, 519, 1930), and Butler and Thomson (unpublished) for determining the partial vapour pressures of the components of aqueous mixtures of the lower aliphatic alcohols.

This method depends upon the fact that, if air is bubbled through a solution under conditions such that equilibrium is attained, then the quantity of each volatile component in the vapour is proportional to its partial vapour pressure in the solution.

If a volume of dry air V, be passed through the solution of methyl alcohol in water at a pressure P, and a temperature T, and if the weight of water removed as vapour be w_w, and the weight of alcohol removed as vapour be w_a, then the volume of water in the saturated vapour is,

$$v_w = w_w \times 22400\ (273 + T) \times 760 / M_w \times 273 \times P \text{ c.cs.} \qquad \text{----------(7)}$$

and the volume of alcohol,

$$v_a = w_a \times 22400\ (273 + T) \times 760/M_a \times 273 \times P \text{ c.cs.} \quad \ldots\ldots\ldots\ldots(8)$$

where M_w and M_a are the molecular weights of water and methyl alcohol respectively. The total volume of the saturated air at pressure P, and temperature T is therefore $V + v_w + v_a$ and, if the vapour obeys the ideal gas laws, according to Dalton's Law of Partial Pressures, the partial pressures of water and alcohol in the vapour are,

$$p_w = v_w \times P/(V + v_w + v_a) \ldots\ldots\ldots\ldots(9)$$

$$p_a = v_a \times P/(V + v_w + v_a) \ldots\ldots\ldots\ldots(10)$$

Any errors arising in the calculation, due to any of the assumptions made, have been fully discussed by Shaw and Butler (loc. cit.) and were considered negligible.

The problem of estimating the relative proportions of alcohol and water in the small quantity of condensate available was overcome by using a Zeiss Industrial Interferometer calibrated with solutions containing known proportions of alcohol and water. In the method finally adopted the condensate was diluted by a known amount so that every unknown solution lay within a certain range of composition over which the instrument was calibrated.

II. PREPARATION OF MATERIALS.

Methyl alcohol.

The commercial methyl alcohol was found to contain a trace of formaldehyde and a considerable quantity of acetone in addition to water. The amount of acetone present was estimated by titration with iodine solution according to the method outlined in Allan's Commercial Organic Analysis, Volume I, p. 109 and found to be about ·15%. The acetone was then removed by the adaptation of Messinger's method outlined by Hartley (J. Chem. Soc., 73, 402, 1923). In this method the acetone was converted into iodoform by shaking 500 c.cs. of N sodium hydroxide solution to which was added, in successive small quantities, 1 litre of the alcohol containing 25 gms. of iodine. On standing for 12 hours the precipitated iodoform was filtered off and the remaining dissolved iodoform removed by refluxing the alcohol mixture on a water bath until the smell was absent. The water added during this process was removed by repeated fraction-:ation, using an eight bulb pear rectifying column, until the boiling-point was constant to ·05°C and finally by refluxing over aluminium amalgam, Hartley and Raikes (J. Chem. Soc., 127, 524, 1925). The amalgam was prepared by warming pieces of sheet aluminium with a solution of mercuric chloride in dry ethyl alcohol.

The methyl alcohol was then distilled and the fraction boiling at 64·46°C (corrected) was retained

for experimental purposes in a coloured bottle to prevent photochemical decomposition. The alcohol, when tested with mercuric cyanide, dissolved in 6 N sodium hydroxide, Hartley and Raikes (loc. cit.), gave no precipitate on boiling, indicating the absence of aldehyde and ketone.

$$D_4^{25^\circ} = \cdot 78643 \text{ gm/c.c.}$$

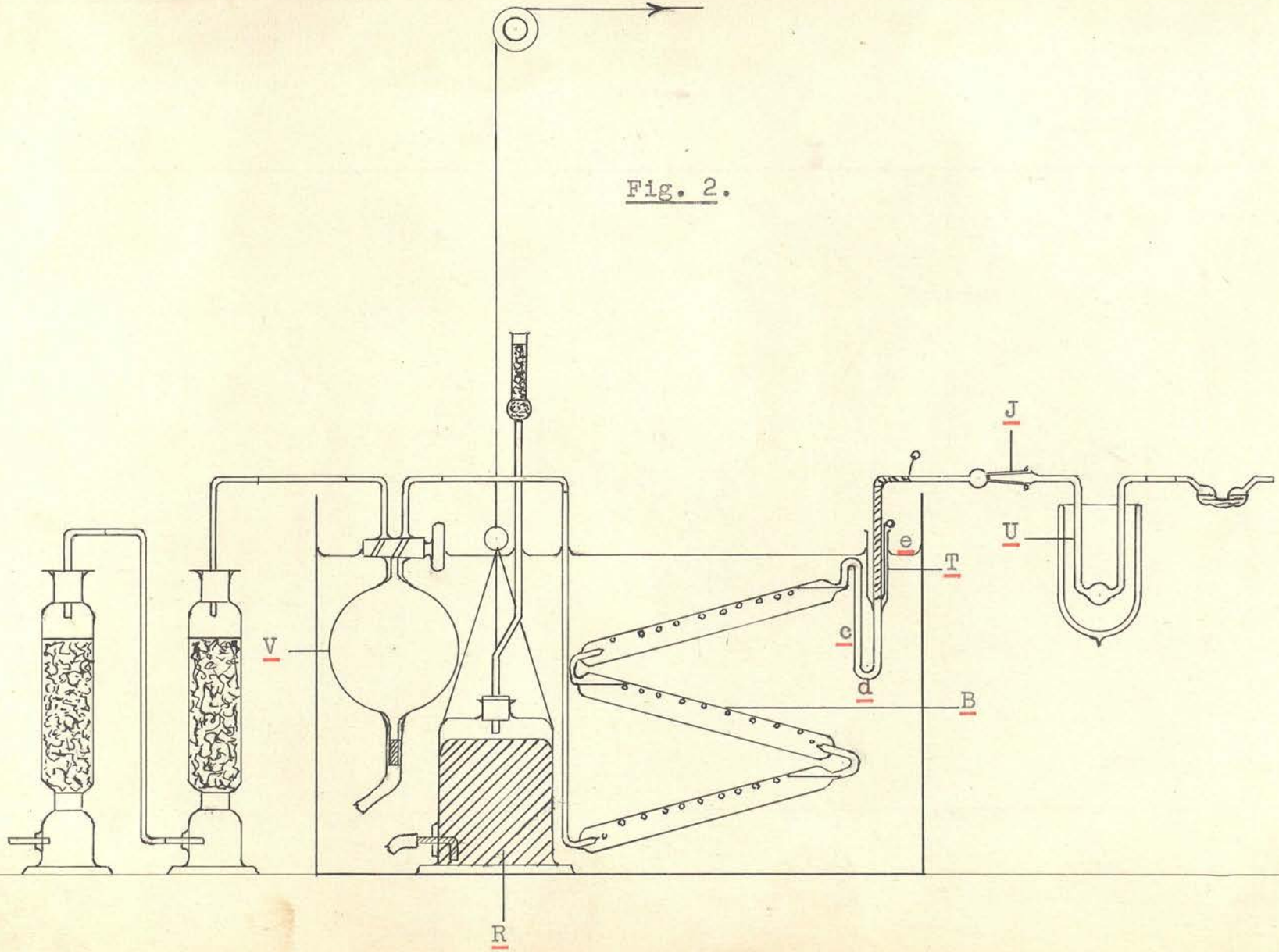
$$N_D^{20^\circ} = 1 \cdot 33083$$

III. APPARATUS AND PROCEDURE.

The air bubbling apparatus (Fig. 2) consisted essentially of three parts (1) a bulb V for measuring a known volume of dry air, (2) a bubbler B for saturating the air with the vapours of methyl alcohol and water from the solution and (3) a collecting tube in which the vapours were condensed and their weight and relative proportions determined.

The bulb V was fitted with a two-way stopcock at the top by which it could be put into communication with either the bubbler B or the calcium chloride and soda lime towers. The lower end of the bulb was connected by pressure tubing to a reservoir R containing clean dry mercury and capable of being raised or lowered at will. The bulb had a line etched on its lower exit and the capacity between this line and the stopcock at the top was determined from the difference in weight of the dry bulb, filled with pure water to

Fig. 2.



the etched line, at 25°C, and the dry bulb empty. This was done by submerging the bulb upside down in a thermostat at 25°C so that only the tip of the lower exit tube remained above the water. The two-way stopcock was closed and the two exit tubes plugged with rubber caps to prevent the ingress of water. Pure water was then poured into the bulb up to the etched line. After removing the rubber caps and carefully drying the bulb externally, it was weighed. The weight of water contained in the bulb at 25°C was 1591·66 gms., being the mean of three reproducible values. The density of water at 25°C was assumed to be 1·00293 ml./gm. (Int. Crit. Tables) giving the volume of the bulb as 1596·33 c.cs.

The bubbler B consisted of three tubes fused together at a small angle of inclination to each other, and each containing a jet to produce a stream of small bubbles of air through any solution contained therein. Owing to the tubes being nearly horizontal the bubbles passed very slowly through each solution and so complete saturation was ensured. This was evident from the fact that reproducible results were obtained in every case even with greatly different rates of flow of air through the solution. Any droplets of liquid entrained in the air were precipitated by passing the vapours round a sharp bend in the exit tube of the bubbler as at cde. In order to prevent condensation of the vapours in the exit tube after the latter leaves the water in the thermostat, it was heated electrically by elements

wound round the tube from a point below the water level e. This was made possible by sealing a wide tube T on to the exit tube below the water level and winding the heating element down into it. The tube T also served to prevent a cold stream of air, caused by convection, impinging upon the bubbler just at the water level e. Prior to fitting tube T, this stream of cold air was the cause of some condensation at the point e. The horizontal portion of the exit tube was heated by means of an electric heating mat laid upon it and bent round it. The end of the exit tube was fitted with a universal ground glass joint J and the entrance tube with a short piece of rubber tubing for connecting to the two-way stopcock on the bulb V. The volume of the bubbler was about 250 c.cs. so that the small quantities of liquid removed by evaporation did not appreciably alter the composition of the solution.

The universal ground glass joint J served to connect the bubbler to a collecting tube U immersed in a mixture of carbon dioxide snow and ether contained in a Dewar flask. This mixture was in the form of a sludge and, therefore, in good heat contact with the collecting tube. This fact coupled with the low temperature of the mixture, about $-80^{\circ}C$, ensured complete condensation provided the rate of bubbling did not exceed a certain limit found experimentally. The limit was determined by

attaching weighed absorption tubes and a sulphuric acid pulsimeter to the collecting tube exit. Condensation was found to be complete when the rate of bubbling through the pulsimeter did not exceed one bubble every two seconds. The pulsimeter was always connected to the collecting tube during the experiments in order to regulate the rate of bubbling and to prevent the entry of moisture.

The bulb V and bubbler B were immersed in a glass-sided thermostat electrically heated and controlled to a temperature of 25 ± ·01°C. The reservoir R could be raised out of or lowered into the thermostat by means of a cable rigged over a pulley and connected to a winding device.

All solutions were made up by weight from the pure alcohol and water, kept in flasks, with rubber stoppers covered with tin-foil and stored in a darkened cupboard. Each solution was run as quickly as possible into the bubbler from a separating funnel arranged to prevent evaporation of the readily volatile methyl alcohol. The bubbler was then immersed and clamped in position in the thermostat, connected to the air vessel V, which had been filled with dry, carbon dioxide-free air, and the heating elements and mat switched on to the mains. After a few minutes to allow the tubes to heat, a stream of air was made to pass slowly through the solution for 10 minutes, to saturate the solution with air and ensure that the conditions at the beginning of

the experiment would be the same as those at the end. Meanwhile the collecting tube was cleaned and dried, allowed to stand in the balance case for half-an-hour and weighed with a ground glass stopper in the junction end. A calcium chloride tube was now connected to the other end and the tube immersed in the freezing mixture. Dry air was thus drawn into the tube on cooling.

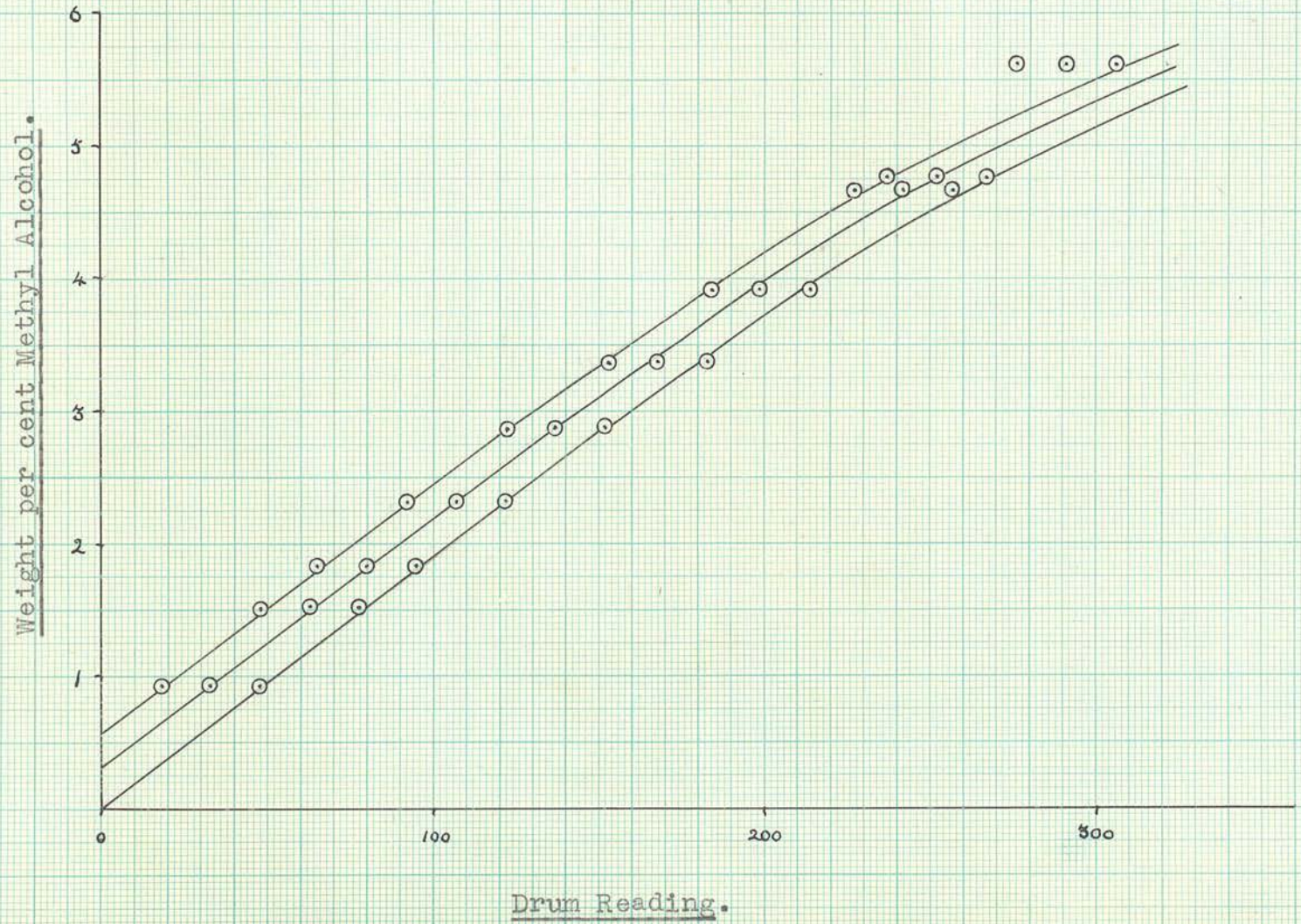
The preliminary bubbling was now stopped, the collecting tube connected to the bubbler and all heating mats and elements switched on so that all exposed portions of the tube were well heated before beginning the experiment. With the air vessel V in communication with the calcium chloride and soda lime towers, the mercury level was adjusted to the etched line on the bottom exit, by means of the reservoir R. The tap was now closed and the reser-:voir raised slightly. The air in vessel V was now allowed to pass slowly through the bubbler, the reservoir being gradually raised as the experiment proceeded, to maintain the pressure head necessary to pass the air through the solution. At the end of the experiment, which took some 5 hours to complete, that is, when the mercury level in the vessel V had reached the bore of the stopcock at the top, the collecting tube was disconnected, stoppered at the junction end and allowed to attain room temperature. After careful cleaning and drying and standing in the balance case for half-an-hour, it was weighed.

The amount of condensate so obtained was, in most cases, insufficient for the easy determination of the relative proportions of alcohol and water. To obtain sufficient condensate for this purpose, the bubbler was connected, through the purifying towers, to an aspirator capable of delivering at least 10 litres of air. The air was passed through the solution at the same rate as in the previous experiment, but 24 hours were required to obtain sufficient condensate. The weight of condensate having been determined, it was carefully washed out of the tube into a tared, stoppered flask, some 20 c.cs. of water being used in successive small quantities at a time, and finally, the flask and contents weighed. The solution so obtained was then compared with pure water in three cells of the interferometer, $\frac{1}{2}$ cm., 1 cm. and 5 cms. in length, the drum reading being taken for three samples of the solution in the case of each cell. The readings so obtained were found to be reproducible.

The interferometer cell consisted of two compart-:ments, L and R. The liquid of lower refractive index was always put into the compartment R and the liquid to be examined in the compartment L. The alcohol solutions were more refractive than water so the latter was chosen as the standard liquid throughout the series of experiments. To obtain a drum reading for any solution, water was introduced into compartment R and the solution into compartment L and the cell placed in position in the interferometer.

Fig. 3.

$\frac{1}{2}$ cm. cell.



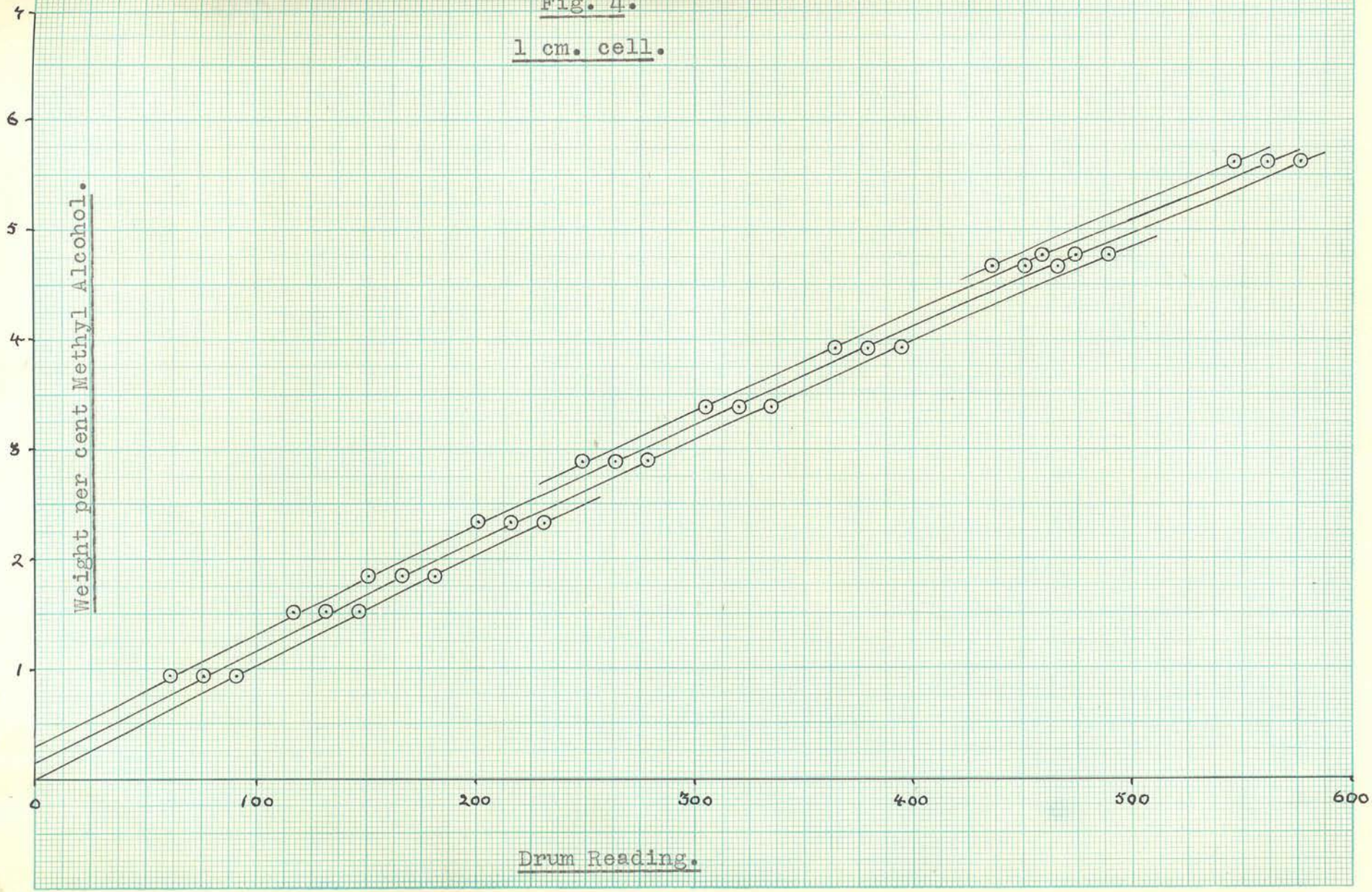
After allowing the liquids to attain the temperature of the water bath, the drum which controls the compensating device, was adjusted until the two sets of fringes coincided. A reading of the position of the drum was then taken by means of the vernier.

The three interferometer cells were calibrated against water as standard, using solutions, made up by weight, ranging from 1% to 9% methyl alcohol in water. Each solution was introduced into compartment L of each of the cells in turn and the drum reading taken for coincidence of the apparent central or achromatic fringe with the standard central fringe. In addition, readings were taken for the coincidence with the standard central fringe of the two fringes adjacent to the apparent central fringe. The readings were repeated three times with fresh samples of each solution. On plotting the drum readings against composition, calibration curves were obtained as shown in Figs. 3, 4 and 5, the calibration curve of each cell consisting of three parallel lines corresponding to the readings of the three fringes observed. The wandering of the true central or achromatic fringe, as explained by L. H. Adams (J.Amer. Chem. Soc., 37, 1189, 1915), made it difficult to plot the calibration curves accurately, especially at high drum readings, without readings for the adjacent fringes.

As can readily be seen, the drum reading of the unknown solution, which was taken for the apparent central fringe only, when interpolated on the

Fig. 4.

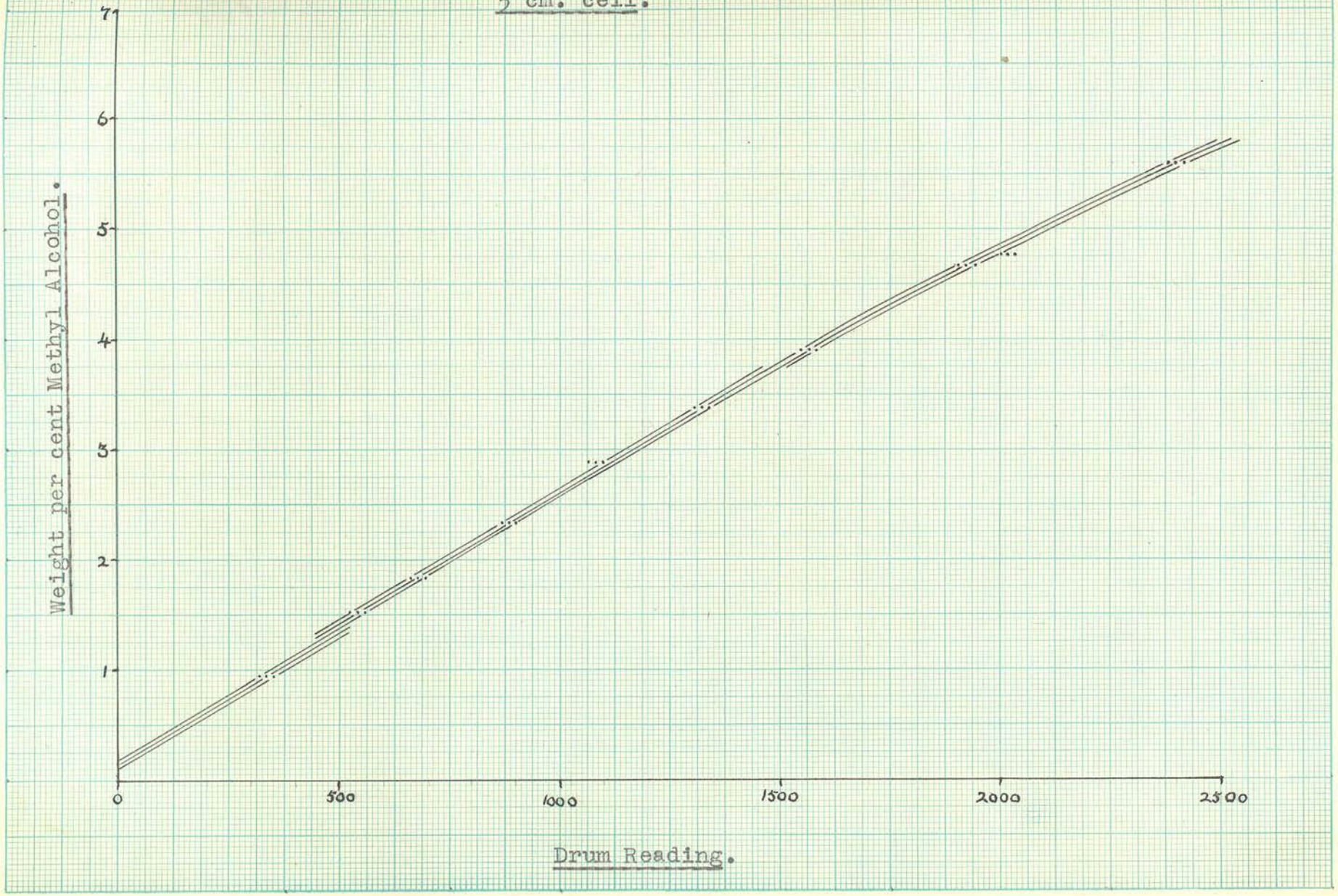
1 cm. cell.



calibration curves, gave three values for the composition in the case of each of the three cells. Scrutiny of the three values obtained for each of the three cells left no doubt as to the correct value of the composition. The $\frac{1}{2}$ cm. cell served to fix the value roughly within wide limits, the 1 cm. to confirm this value more accurately and the 5 cms. cell to give the value with sufficient accuracy for the experiment, see Table 3a. The composition of the diluted solution can be estimated with an accuracy of about ·004% which means that, with a dilution, on an average of 20 to 1, the composition of the condensate can be estimated to ·08%.

An attempt was made to estimate the composition of the condensate directly, using the interferometer and an arbitrary standard solution of methyl alcohol in water of nearly the same composition as the unknown. Calibrating with two solutions, one above and one below the composition of the unknown and close to it, the composition of the condensate could be obtained by interpolation on the straight line between the known compositions. The advantages of being able to determine the composition of the condensate directly were offset by some disadvantages overcome by the dilution method. For example, the small quantity of condensate collected, only ·5 gm., precluded the use of the 5 cms. cell, a serious loss in accuracy, whilst it was found to be very difficult to reproduce results owing to the evaporation of methyl alcohol from the cells at concentrations greater than 20%. The

Fig. 5.
5 cm. cell.



dilution method eliminated the evaporation difficulty and provided sufficient bulk of liquid for not only one reading with the 5 cms. cell, but also for several readings with each of the three cells. Again the interferometer calibration curve had a maximum in the region of 50-60% methyl alcohol which meant that any interpolations made on the curve anywhere near this region were inaccurate. In diluting, the steepest portion of the curve was used and this was fully explored by one set of calibration solutions.

The experiment was repeated with each solution until two reproducible values of the partial vapour pressures were obtained.

IV. EXPERIMENTAL DATA.

The calibration figures of the three interferometer cells are given in Table 2, the middle figure under "drum readings" corresponds to the apparent central fringe, and the figures on each side to the adjacent fringes.

Table 2.

Wt%. Methyl Alcohol.	DRUM READINGS. ½ cm. cell.	1 cm. cell.	5 cm. cell.
0·944	18, 33, 48.	61, 76, 91.	323, 338, 353.
1·513	48, 63, 78.	117, 132, 147.	521, 536, 551.
1·847	65, 80, 95.	151, 166, 181.	661, 676, 691.
2·341	92, 107, 122.	201, 216, 231.	864, 879, 894.
2·880	122, 137, 152.	248, 263, 278.	1082,1097,1112.
3·383	153, 168, 183.	305, 320, 335.	1309,1324,1339.
3·909	184, 199, 214.	364, 379, 394.	1550,1565,1580.
4·670	227, 242, 257.	436, 451, 466.	1905,1920,1935.
4·761	237, 252, 267.	459, 474, 489.	2000,2015,2030.
5·608	276, 291, 306.	553, 568, 583.	2381,2396,2411.
9·067	493, 508, 523.	961, 977, 992.	- - -

The full experimental details of the examination of the 65·79% alcohol solution are given in Table 3a. The two sets of figures correspond to the two determinations made with this solution. N_a is the composition of the solution expressed in moles per cent methyl alcohol, w_1 is the weight in gms. of condensate obtained by passing the known volume of air (1596·33 c.cs.) through the solution, w_2 is the weight in gms. of condensate obtained for composition purposes, P is the mean atmospheric pressure during the experiment, expressed in m.ms. of mercury, M is the weight in gms. of the diluted mixture, C is the composition of the condensate in weight per cent methyl alcohol, p_a and p_w are the partial vapour pressures of alcohol and water respectively, in m.ms. of mercury.

Table 3a.

	Determination I.		Determination II.
N_a	65·79		65·79
W_1	0·2891		0·2894
P	751·25		742·50
W_2	0·6278		0·2894
M	17·8350		12·0361
Interferometer readings:-			
½ cm. cell.	161		117
1 cm. cell.	309		209
5 cm. cell.	1302		842
Composition of M:-			
½ cm. cell.	3·03, 3·28, 3·50		1·93, 2·25, 2·53
1 cm. cell.	3·15, 3·29, 3·41		2·13, 2·25, 2·28
5 cm. cell.	3·26, 3·29, 3·33		2·22, 2·25, 2·29
C	93·47		93·58
Mean C		93·53	
p_a	85·73		85·69
p_w	10·54		10·54
Mean p_a		85·71	
Mean p_w		10·54	

The three figures given for the composition of M with each cell are those obtained from the triple calibration curve and as can be seen, the middle figures only are in agreement and were, therefore, taken as representing the correct value of the composition.

The experimental results for the whole series of solutions are given in Table 3b, the symbols used having the same significance as above. Duplicated results are given for each solution, the mean being taken of the partial pressures calculated for each determination.

Table 3b/

Table 3b.

N_a	w.	Mean. C.	P.	p_a	p_w	Mean values. p_a	Mean values. p_w
2.02	0.0477	22.97	755.25	3.85	22.92	3.85	22.90
	0.0476		759.00	3.84	22.88		
4.03	0.0577	37.95	759.00	7.65	22.24	7.67	22.28
	0.0579		758.50	7.68	22.32		
6.20	0.0699	48.50	763.25	11.78	22.24	11.76	22.19
	0.0696		759.25	11.73	22.14		
7.91	0.0780	55.80	755.50	15.07	21.23	15.07	22.23
	0.0780		752.25	15.07	21.22		
11.45	0.0973	64.37	749.00	21.49	21.14	21.49	21.15
	0.0974		738.75	21.49	21.15		
20.17	0.1386	76.58	760.13	35.80	19.47	35.83	19.49
	0.1389		757.25	35.86	19.50		
39.73	0.2093	87.05	750.00	59.61	15.76	59.63	15.76
	0.2095		746.50	59.64	15.76		
65.79	0.2894	93.53	742.50	85.69	10.54	85.71	10.54
	0.2891		751.25	85.73	10.54		
81.37	0.3469	96.71	742.00	103.85	6.28	103.85	6.28
100.00	0.4179	100.00	758.70	126.63	-		
	0.4198		750.00	126.86	-	126.68	-
	0.4197		746.00	126.55	-		

Fig. 6.

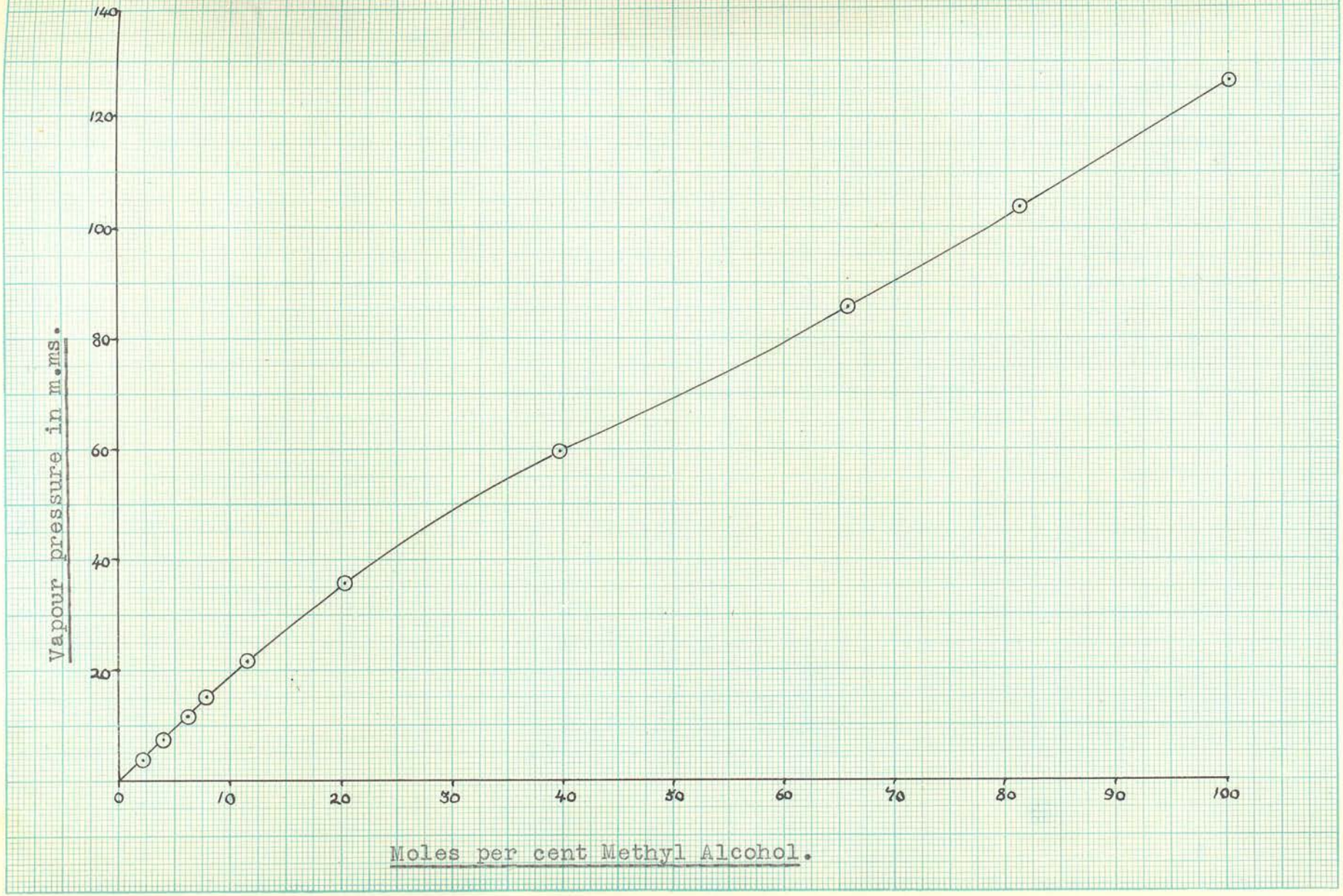

140
120
100
80
60
40
20
Vapour pressure in m.ms.
0
10
20
30
40
50
60
70
80
90
100
Moles per cent Methyl Alcohol.

Fig. 6 shows the variation of the partial vapour pressure of methyl alcohol with the mole percentage of alcohol in solution, and Fig. 7 shows the corresponding variation of the partial vapour pressure of water.

In Table 4 are given the values of the activities and activity coefficients of the alcohol and water in the various solutions examined. N_a is expressed as the mole fraction of alcohol in solution, p_a and p_w are the mean partial vapour pressures, a_a and a_w the activities and f_a and f_w the activity coefficients respectively of the alcohol and water.

Table 4/

Fig. 7.

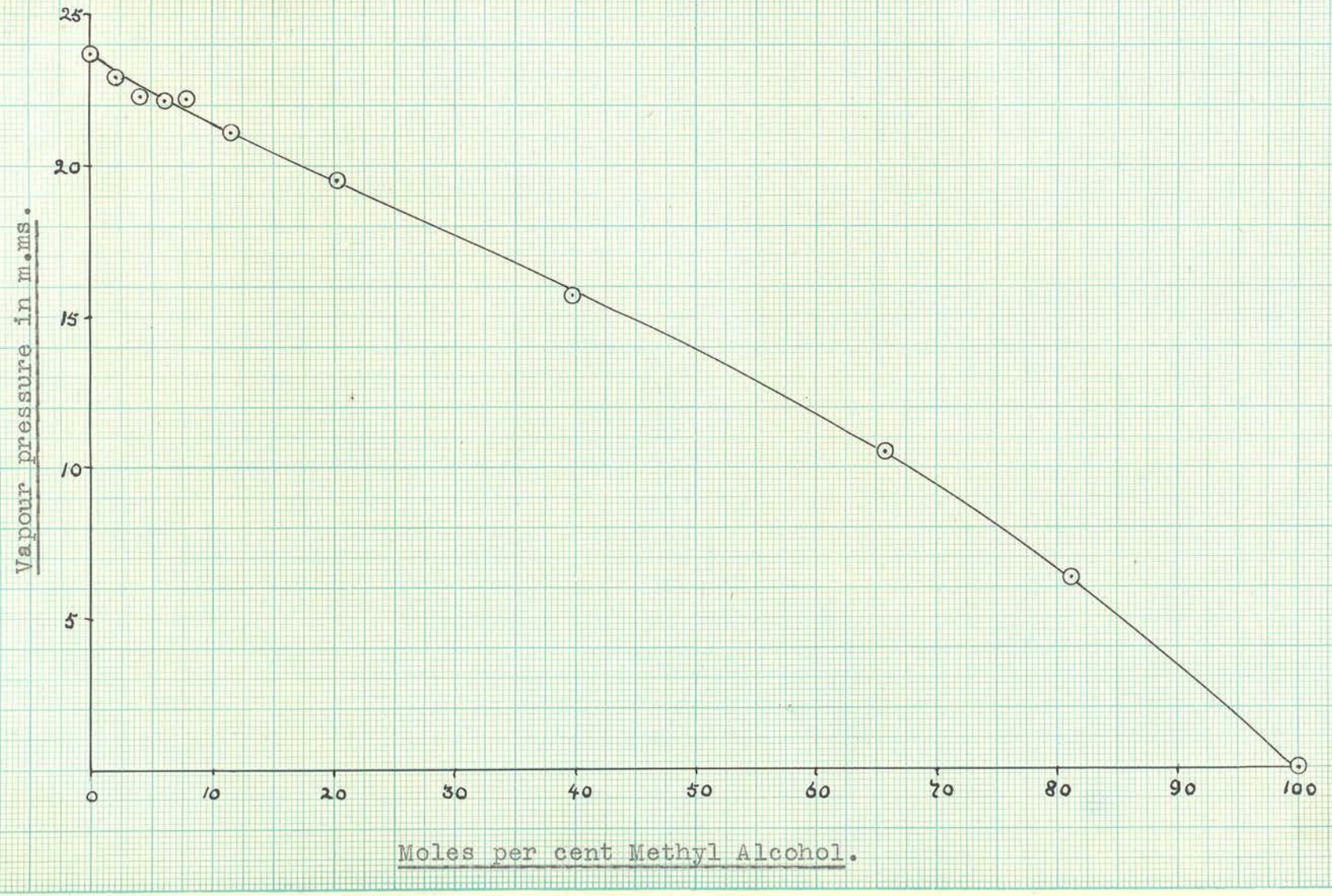
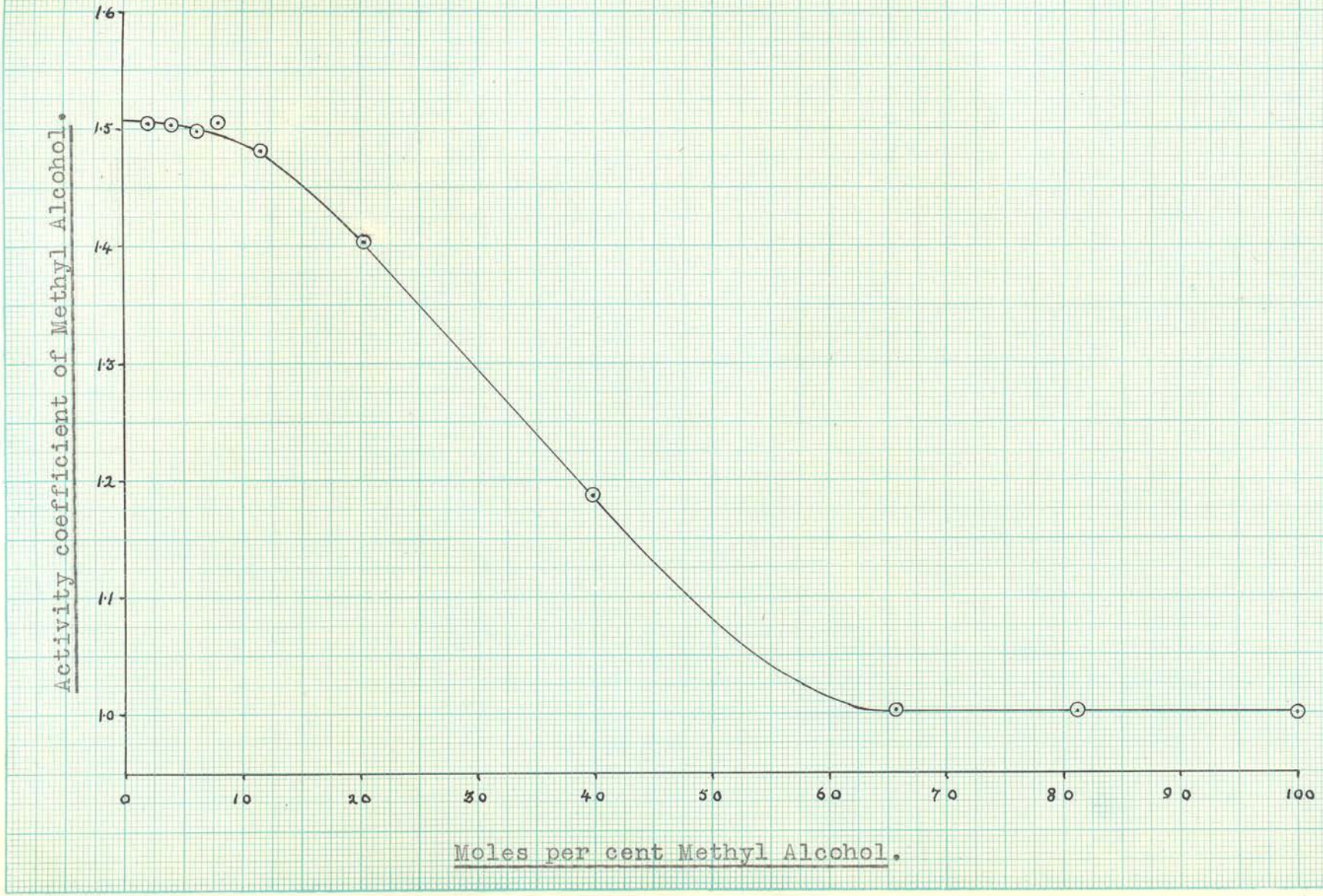

25
20
15
10
5
Vapour pressure in m.ms.
0
10
20
30
40
50
60
70
80
90
100
Moles per cent Methyl Alcohol.

Table 4.

N_a	p_a	$a_a = p_a/p_a^\circ$	f_a	p_w	$a_w = p_w/p_w^\circ$	f_w
0·00	0·00	0·00	0·00	23·76	1·0000	1·000
0·0202	3·85	0·0304	1·505	22·90	0·9663	0·984
0·0403	7·67	0·0606	1·503	22·28	0·9377	0·977
0.0620	11·76	0·0929	1·498	22·19	0·9339	0·996
0·0791	15·07	0·1190	1·505	22·23	0·9356	1·016
0·1145	21·49	0·1697	1·482	21·15	0·8901	1·005
0·2017	35·83	0·2830	1·403	19·49	0·8203	1·028
0·3973	59·63	0·4710	1·186	15·76	0·6633	1·101
0·6579	85·71	0·6770	1·029	10·54	0·4436	1·297
0·8137	103·85	0·8203	1·008	6·28	0·2643	1·419
1·0000	126·68	1·00	1·000	0·00	0·00	0·00

Fig. 8.


Activity coefficient of Methyl Alcohol.
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0
10
20
30
40
50
60
70
80
90
100
Moles per cent Methyl Alcohol.

In Fig. 8 the values of the activity coefficient of methyl alcohol are plotted against the mole fraction of alcohol in solution and in Fig. 9 is the corresponding plot for water.

On extrapolating the curve in Fig. 8 to the axis $N_a = 0$ the value of f_a° is obtained, that is, the value of the activity coefficient of methyl alcohol at infinite dilution.

The value so extrapolated is $f_a^{\circ} = 1{\cdot}507$ which when introduced into the equation for the free energy difference gives:-

$$F_a^{\circ'} - F_a^{\circ} = 243 \text{ calories.}$$

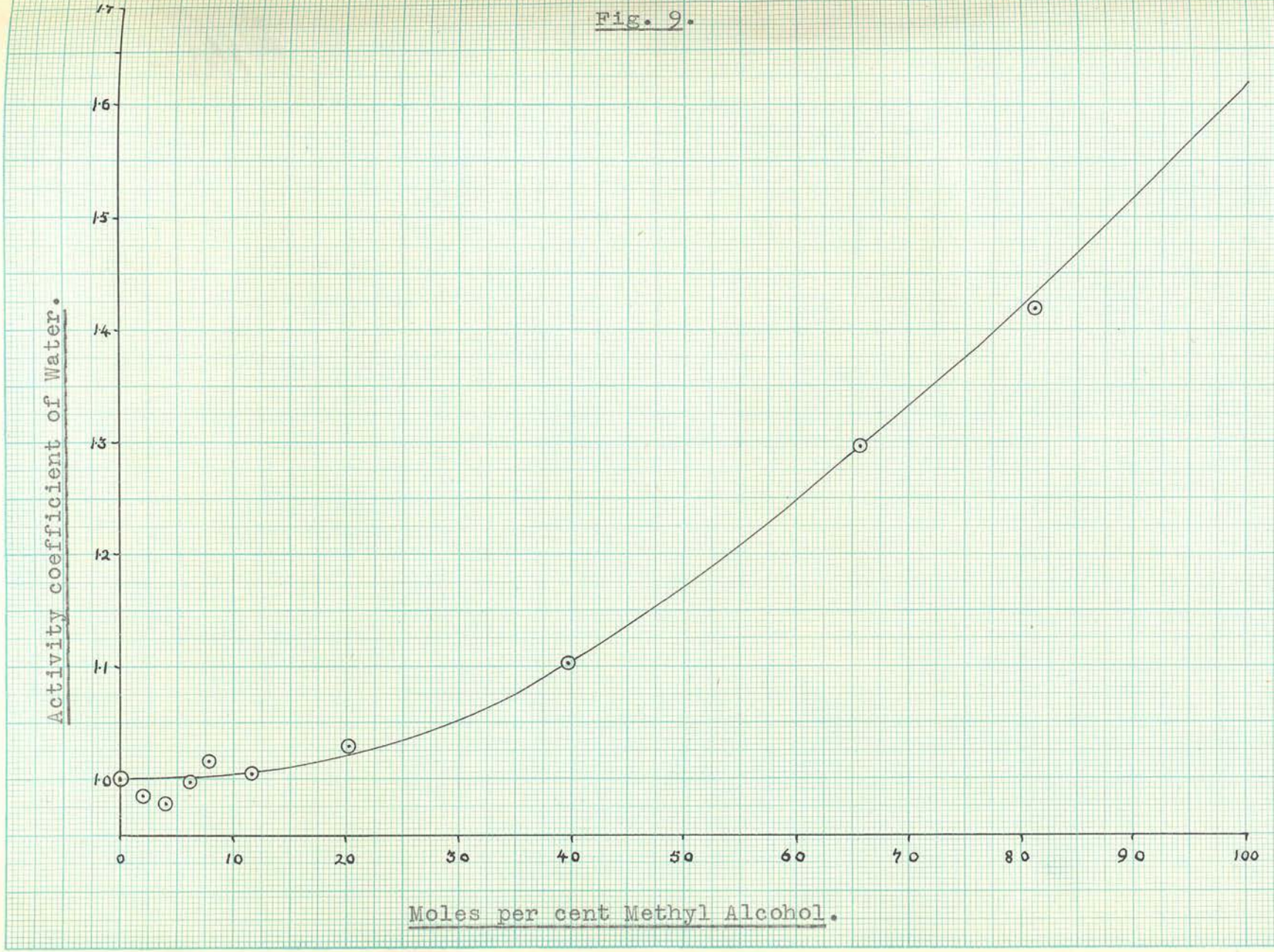
In a similar manner it is possible to determine the value of f_w°, the activity coefficient of water in infinitely dilute solutions of water in alcohol, and so obtain the value of the free energy difference for water in methyl alcohol solution.

The value of f_w°, extrapolated on Fig. 9, is 1·62, and the value of the free energy difference is:-

$$F_w^{\circ'} - F_w^{\circ} = 287 \text{ calories.}$$

The activity coefficients of water in the dilute solutions containing up to ·062 mole fraction of alcohol are slightly less than unity. These values are undoubtedly low, for the activity coefficients of the alcohol in these solutions indicate that the values of f_w should be very close to unity. The maximum error is thus of the order of 2%. Considering the indirect estimation of the composition of the condensate, this error is not unreasonably large.

Fig. 9.


1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
Activity coefficient of Water.
0
10
20
30
40
50
60
70
80
90
100
Moles per cent Methyl Alcohol.

The methyl alcohol system has proved to be the most difficult of the studies of alcohol-water solutions which have been made in this laboratory.

Part I (B).

The solubilities of n-amyl, n-hexyl, n-heptyl, n-octyl alcohols in water.

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INTRODUCTION.

The vapour pressures of the alcohols above n-butyl alcohol in the aliphatic series of alcohols, are very low - that of n-butyl alcohol is only 6·96 m.m., Thomson (loc. cit.) - so that accurate determinat-:ions of their partial vapour pressures become increas-:ingly difficult. In addition, their solubilities in water decrease very rapidly with increasing molecular weight thereby greatly reducing the accessible range of solutions for examination and thus limiting the portion of the vapour pressure curve capable of investigation. The determination of the free energy difference of the higher members of the series, by measurements of the partial vapour pressures, is therefore impracticable.

When the alcohol and water are not completely miscible, the activity of the alcohol must be the same in the two phases in equilibrium with each other or

$$f_a \times N_a^s = f_a' \times N_a^{s'} \quad \text{.....(11)}$$

where f_a is the alcohol activity coefficient in the aqueous phase.

N_a^s is the mole fraction of alcohol in the aqueous phase.

f_a' is the alcohol activity coefficient in the alcohol phase.

$N_a^{s'}$ is the mole fraction of alcohol in the alcohol phase.

Thus the activity coefficient of the alcohol in the aqueous layer is given by

$$f_a = f_a' \times N_a^{s'} / N_a^s \quad \text{.....(12)}$$

If the alcohol phase contains only a small proportion of water the activity of the alcohol can be taken as unity and,

$$f_a = {}^1/_{N_a^s} \quad \ldots\ldots\ldots\ldots\ldots\ldots(13)$$

If the aqueous layer is also a dilute solution the value of f_a approaches f_a^o the value of the activity coefficient in very dilute solution and we have,

$$f_a^o = {}^1/_{N_a^s} \quad \ldots\ldots\ldots\ldots\ldots\ldots(14)$$

Substituting this value of f_a^o in the equation

$$F_a^{o'} - F_a^o = RT \log f_a^o$$

given in Part I (A) of this thesis we have

$$F_a^{o'} - F_a^o = - RT \log N_a^s \ldots\ldots\ldots(15)$$

The errors introduced by the above approximations compensate each other to some extent as can be shown by considering the data, obtained by Thomson (loc. cit.) for butyl alcohol.

Solubility determinations show that the mole fraction of alcohol in the alcoholic phase is only ·488, very much lower than that required by the assumption made above. The value of ${}^1/_{N_a^s}$ derived from the mole fraction of alcohol in the water phase is 53·1. Vapour pressure determinations give a value of f_a^o equal to 46·5 which does not differ greatly from the value of ${}^1/_{N_a^s}$. This difference would be less for the higher alcohols and the values of the free energy difference given with sufficient accuracy by

equation (15).

This method of evaluating ($F_a^{o'} - F_a^{o}$) has been successfully applied by Butler (Proc. Roy. Soc., 135A, 365, 1932), to a series of esters of aliphatic acids whose solubilities were determined by Sobotka and Kahn (J. Amer. Chem. Soc., 53, 2935, 1931).

It was decided to make use of equation (15) to determine the free energy differences of the higher members of the aliphatic series of alcohols and so complete the investigation of the hypothesis cited in Part I (A) of this thesis. The members to be investigated are n-amyl, n-hexyl, n-heptyl and n-octyl alcohols in aqueous solution at 25°C.

An examination of the literature revealed no reliable figures for the solubilities of these alcohols in water at 25°C.

EXPERIMENTAL.

I. Method of Experiment.

The methods of determining the solubility of a liquid in a liquid have been roughly divided into two classes viz. "synthetic" and "analytic" by Rothmund (Z. phys. Chem., 26, 443, 1898). A synthetic method was defined as one in which the pure components were mixed until saturation was reached and the solubility given by the relative amounts required to produce saturation under the required conditions. In an analytic method the saturated phases were analysed for the relative proportions of each component. A survey of the literature showed that, in the relatively

few determinations made of the solubilities of liquids in liquids, the synthetic method has been used more frequently.

The most important synthetic method was that introduced by Alexejew (Wied. Ann., 28, 305, 1886), and used later by Klobbie (Z. phys. Chem., 24, 615, 1897), Schreinmakers (Z. phys. Chem., 27, 97, 1898), Fontein (Z. phys. Chem., 73, 212, 1910), Sidgwick (J. Chem. Soc., 99, 1122, 1911), and Thomson (loc.cit.) for binary mixtures.

The method consisted in heating and cooling different known mixtures of the two liquids and observing the temperature at which homogeneity appeared and disappeared. By plotting this critical temperature against the composition of the mixtures and interpolating at the desired temperature, a value was obtained for the composition of the mixture saturated at this temperature. This was the solubility required. In many cases, the determinations were very accurate, the turbidity point being detected to within less than $\cdot 1^{\circ}C$ but, in other cases, there was little or no tendency to form an emulsion and results were inaccurate or impossible. Sidgwick and Thomson found little difficulty in obtaining reproducible results, but Klobbie found it necessary to use a dye to indicate the change from homogeneity to heterogeneity. A few preliminary trials with the alcohols to be examined served to show that the critical point was very difficult to detect.

The solubility of amyl alcohol in water at 22°C has been determined by Herz (Berl. Ber., 31, 2671, 1898) using a synthetic method, similar to an ordinary acidimetric titration, in which the alcohol was run into a known amount of water until saturation was attained. The difficulty was again that of detecting the end point at which the two phase system just appeared. Hill (J. Amer. Chem. Soc., 45, 1143, 1923) has shown that similar work by Herz on the solubility of ether in water was very inaccurate. The titration method has been used with great success by Sobotka and Kahn (loc. cit.), for estimating the solubilities of sparingly soluble esters in water. The ester was stained with a suitable dye insoluble in water, and titrated into a known volume of the latter maintained at the desired temperature. The dye served to indicate the saturation point. Although considerable accuracy was claimed and the presence of the dye considered to affect the solubility as negligibly as an indicator the stoichiometric relations in an ordinary titration, it is possible that, in very dilute solutions, the dye may appreciably affect the solubility.

Wilson (J. Amer. Chem., Soc., 43, 704, 1921) has reviewed the situation with regard to estimating the amount of water in mixtures with iso-amyl alcohol. Such an estimation was a typical analytic method of solubility determination. The review pointed out that the chemical method of analysis was toocumbersome and complicated of technique, whilst, of the physical

methods, a colorimetric was rejected as being insufficiently accurate. The variation of the conductivity of potassium thiocyanate in iso-amyl alcohol mixtures was eventually used as the basis of analysis. Although its accuracy cannot be doubted, the application of conductivity variations to the present research was considered to be too complicated.

Hill (loc. cit.) has obtained the solubilities of several pairs of liquids from volumetric measure-:ments of the two phases after mixing two batches of the two components, having different known compositions. The chief inaccuracy in this method was due to the retention of a thin layer of a phase on the glass of the bulb containing the other phase. The magnitude of this error could not be ascertained, but it was always present. Kablukov and Malischeva (J. Amer. Chem. Soc., 47, 1553, 1925) investigated the solubility of iso-amyl alcohol in water using this method but pointed out that the accuracy depended largely upon the relative weights or volumes of the components in the mixture. Hill and Malisoff (J. Amer. Chem. Soc., 48, 918, 1926) showed that the optimum ratio was equal to the weight distribution ratio of the two components between the two phases. It would appear, therefore, that the method is unsuitable for sparingly soluble liquids which adhere strongly to glass like the higher aliphatic alcohols.

It was finally decided to use an analytic method in which the saturated phase was compared with standard solutions of known composition using the Zeiss

interferometer.

II. PREPARATION OF MATERIALS.

Little information could be obtained upon the subject of purifying the higher aliphatic alcohols although Verkade and Coops (Trav. Chim. des Pays Bas, 46, 905, 1927) describe the preparation of the pure normal alcohols for combustion purposes. It was decided to rely upon fractionation with an efficient rectifying column to purify the "pure" quality samples of the n-amyl, n-hexyl, n-heptyl and n-octyl alcohols supplied by the B. D. H.

A Hempel fractionating column with an effective length of 30 cms. and filled with a mixture of glass beads and rings, was fitted with ground glass joints to take the condenser and distilling flask. The thermometer was arranged to have all the mercury immersed in the vapour and was fitted with a rubber stopper protected with tin-foil. In this way contamination from corks etc., was reduced to a minimum. The n-amyl alcohol was distilled at atmospheric pressure but, because of their high boiling-points, the others were distilled under reduced pressure. All heating was carried out by means of an oil bath.

Each alcohol was fractionated several times until a fraction was obtained whose boiling-point remained constant to $\cdot 1^{\circ}C$, it being found necessary to protect the head of the column with cotton wool to prevent fluctuation due to draughts. The fraction

so obtained was then refluxed over clean metallic calcium for 6 hours to dry it and then distilled. This was once again fractionated and the fractions, whose properties are given in Table 5, were retained for experimental purposes. D is the density at 25°C compared with water at 4°C, n the refractive index at 20°C using the D line, and B.P. is the boiling-point corrected to 760 m.ms. pressure. The densities were taken with a Sprengel type pyknometer and refractive indices with a Pulfrich refractometer.

Table 5.

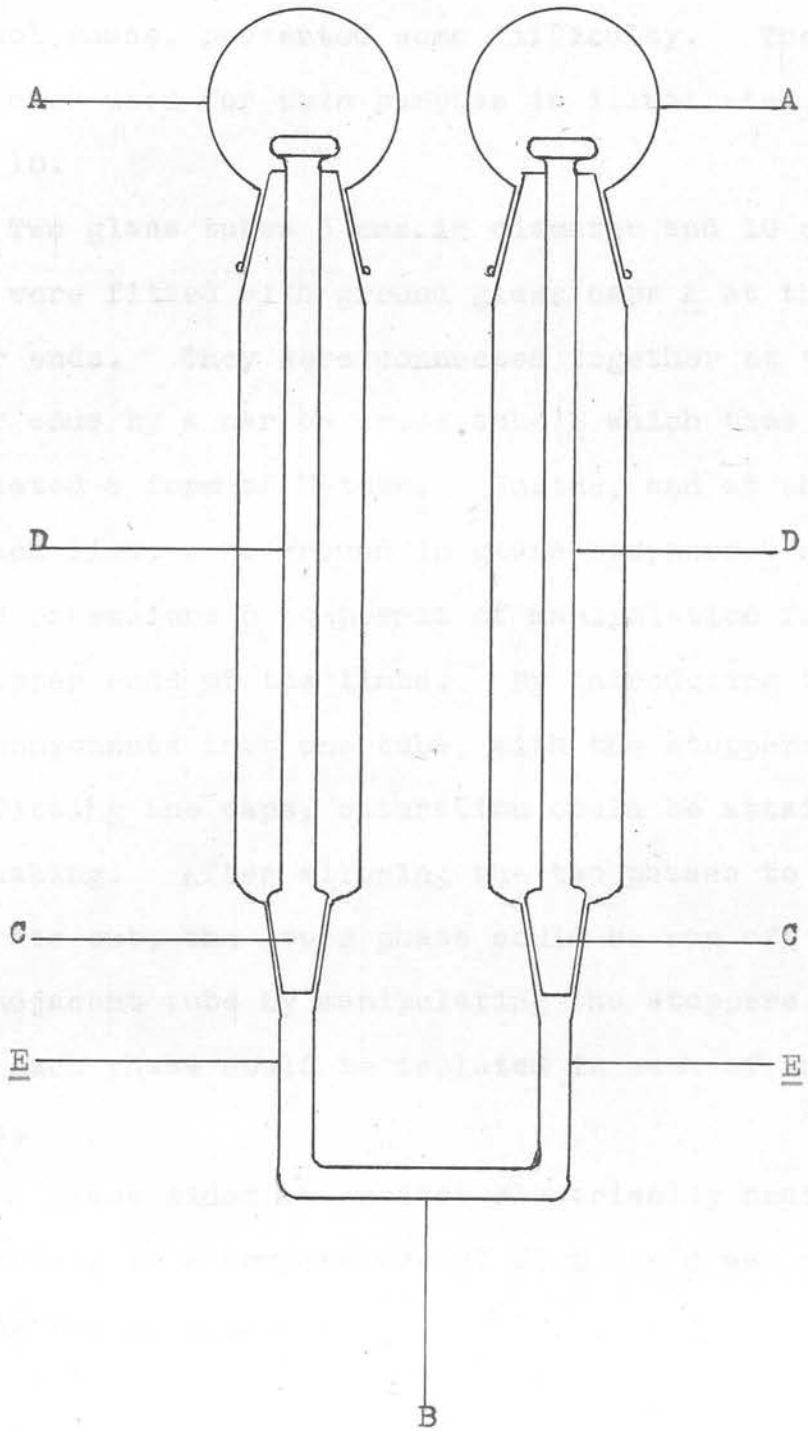
Alcohol.	D	n	B.P.
N-amyl.	0·81146	1·41043	137·65
N-hexyl.	0·81648	1·41778	155·70
N-heptyl.	0·81960	1·42337	175·64
N-octyl.	0·82238	1·42937	194·49

The corresponding values from the Int. Crit. Tables are given in Table 6. The values of D and n are not taken at the same temperature and the value of the latter is inserted where it differs from 25°C.

Table 6.

Alcohol.	D	n	B.P.
N-amyl.	$0\cdot814^{14\cdot4}$	$1\cdot40963^{14\cdot6}$	137·75
N-hexyl.	$0\cdot820^{20}$	-	155·8
N-heptyl.	$0\cdot817^{22}$	$1\cdot42326^{22\cdot4}$	175·8
N-octyl.	$0\cdot827^{20}$	$1\cdot4279^{9\cdot5}$	194

Fig. 10.



III. APPARATUS AND PROCEDURE.

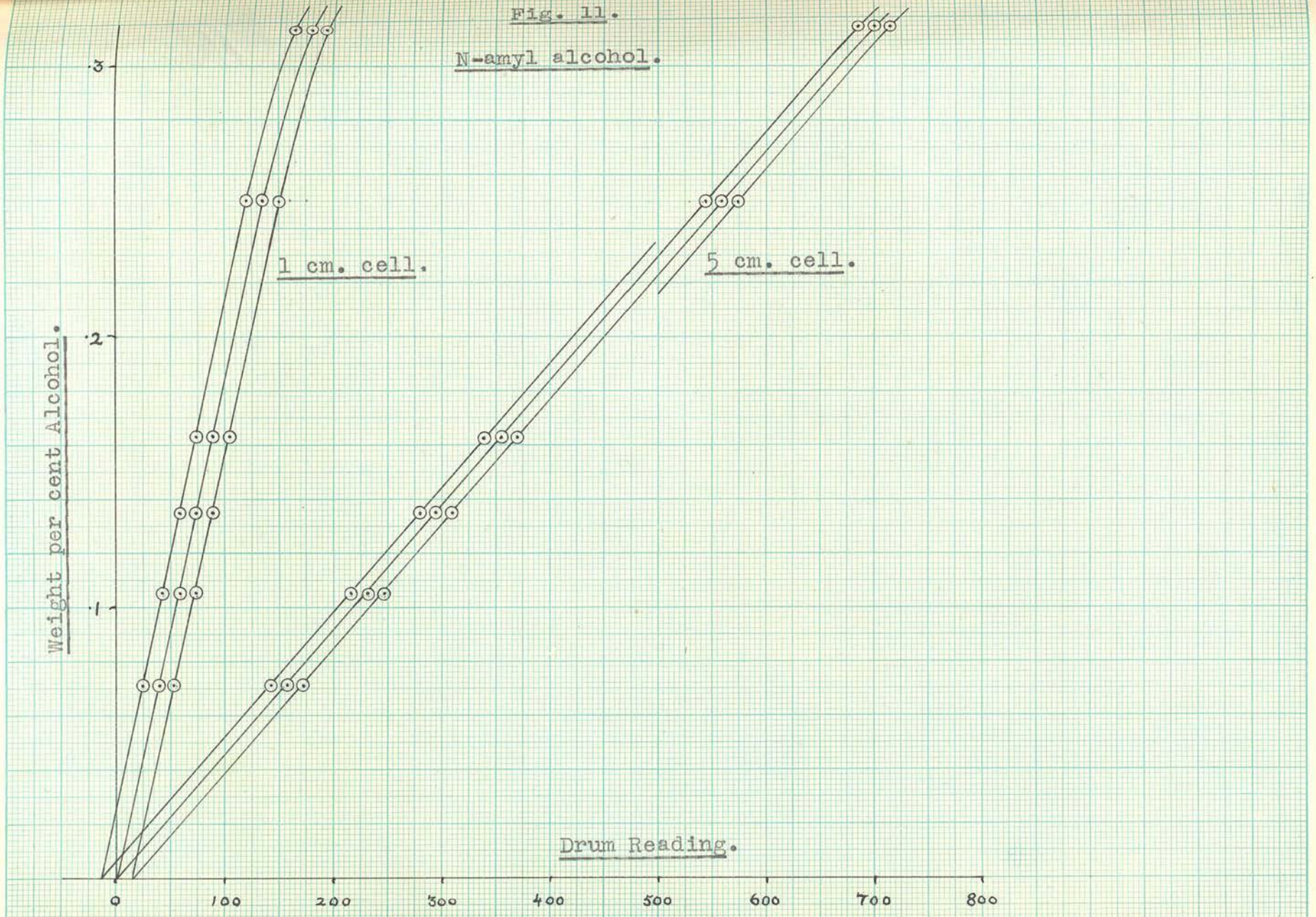
The saturation of the water with the alcohol was carried out in a piece of apparatus designed for the easy separation of the two phases. Although it was easy to saturate the two phases, the removal of a sample of the aqueous layer, the lower one, uncontaminated by undissolved alcohol from the alcohol phase, presented some difficulty. The apparatus used for this purpose is illustrated in Fig. 10.

Two glass tubes 3 cms. in diameter and 10 cms. long were fitted with ground glass caps A at their upper ends. They were connected together at their lower ends by a narrow cross tube B which thus completed a form of U-tube. Inside, and at the foot of each limb, were ground in glass stoppers C with glass extensions D to permit of manipulation from the upper ends of the limbs. By introducing the two components into one tube, with the stoppers in, and fitting the caps, saturation could be attained by shaking. After allowing the two phases to separate out, the lower phase could be run off into the adjacent tube by manipulating the stoppers. Thus each phase could be isolated in each of the limbs.

A glass sided thermostat electrically heated and controlled to a temperature of $25 \pm \cdot 01^{\circ}C$ was used during the experiments.

Fig. 11.

N-amyl alcohol.



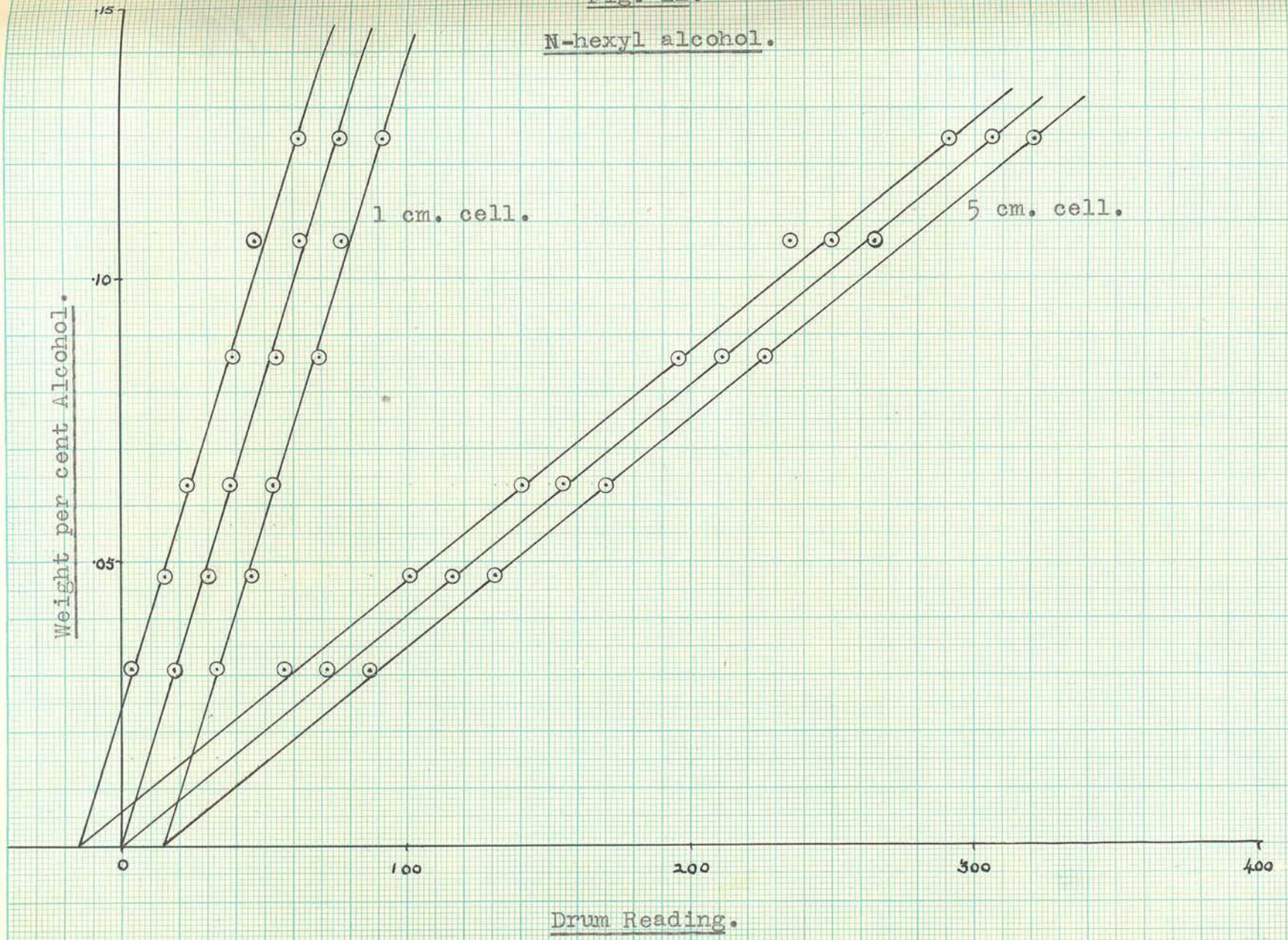
Some 10 c.cs. of water were introduced into one of the stoppered limbs and then a similar amount of alcohol. The caps were put on and the apparatus thoroughly shaken in the thermostat for an hour. It was then left there for 24 hours to allow the phases separate and to make certain that saturation was complete. Only that portion of the apparatus containing the liquids was immersed in the thermostat. With the limbs clamped in this position, the caps were removed along with the stopper from the empty limb. By carefully manipulating the other stopper, the aqueous phase was run into the empty tube without letting any alcoholic phase pass position E in the diagram. The separation of the phases was thus accomplished at the required temperature of 25°C.

About 2 gms. of the water phase were withdrawn and transferred to a tared, stoppered flask and its weight determined accurately. It was then diluted by a known amount and the resulting solution compared with water as standard in the 1 cm. and 5 cms. cells of the interferometer, the drum reading being taken for three samples of solution. The readings so obtained were reproducible.

The interferometer was calibrated in a manner similar to that described in Part I (A) of this thesis. Solutions were made up by weight from water and each of the purified alcohols. These were then compared with water in the interferometer, readings being taken for the central and the two

Fig. 12.

N-hexyl alcohol.



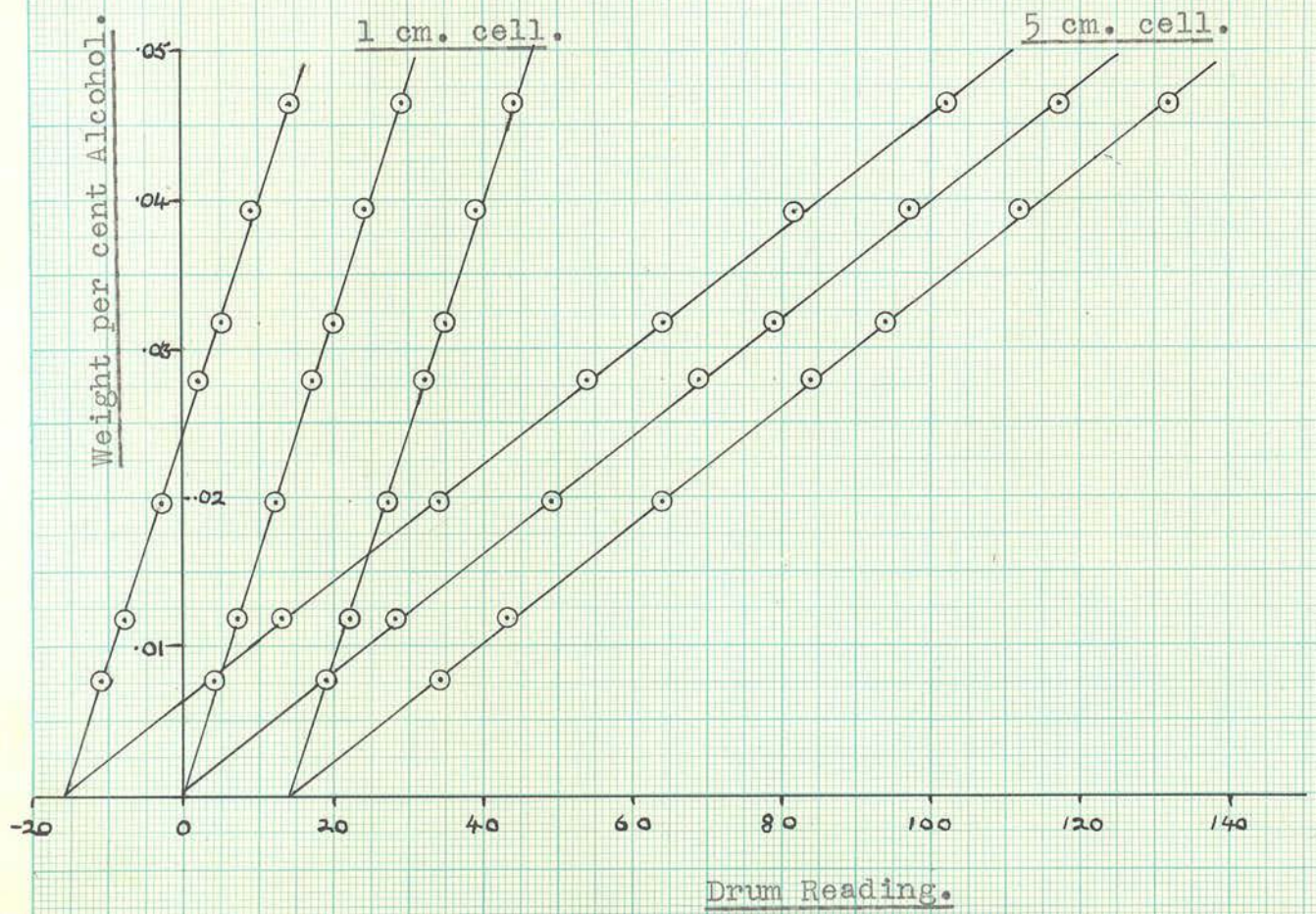
adjacent fringes. The 1 cm. and 5 cm. cells only were used as the $\frac{1}{2}$ cm. cell gave readings which were too small to be of any value. The plots of these readings against the weight percentage of alcohol in solution, are given in Figs. 11, 12, 13 and 14. The curves were linear over the range of concentrations employed and no difficulty was experienced with the wandering of the apparent central fringe. It was found to be very difficult to make up calibration solutions whose compositions approached that of the saturated phase probably due to the fact that, as the alcohol dissolved, it became increasingly difficult to dissolve the diminishing quantity which remained. The cells were, therefore, calibrated for low concentrations only and this necessitated the dilution of the water phase to come within the range used.

When the drum reading obtained for the solution of the water phase, was interpolated on to the triple calibration curves, three values of the composition were estimated for each cell. In any one such estimation, it was found that, of the three values, those derived from the apparent central fringe reading for each cell, were coincident. The correct figure for the composition was thus fixed by a comparison of the figures given by the two cells, the 1 cm. cell serving to fix it roughly and the 5 cm. cell to give the necessary accuracy.

The determinations of the solubility of each of

Fig. 13.

N-heptyl alcohol.



the alcohols were repeated until at least five reproducible values were obtained.

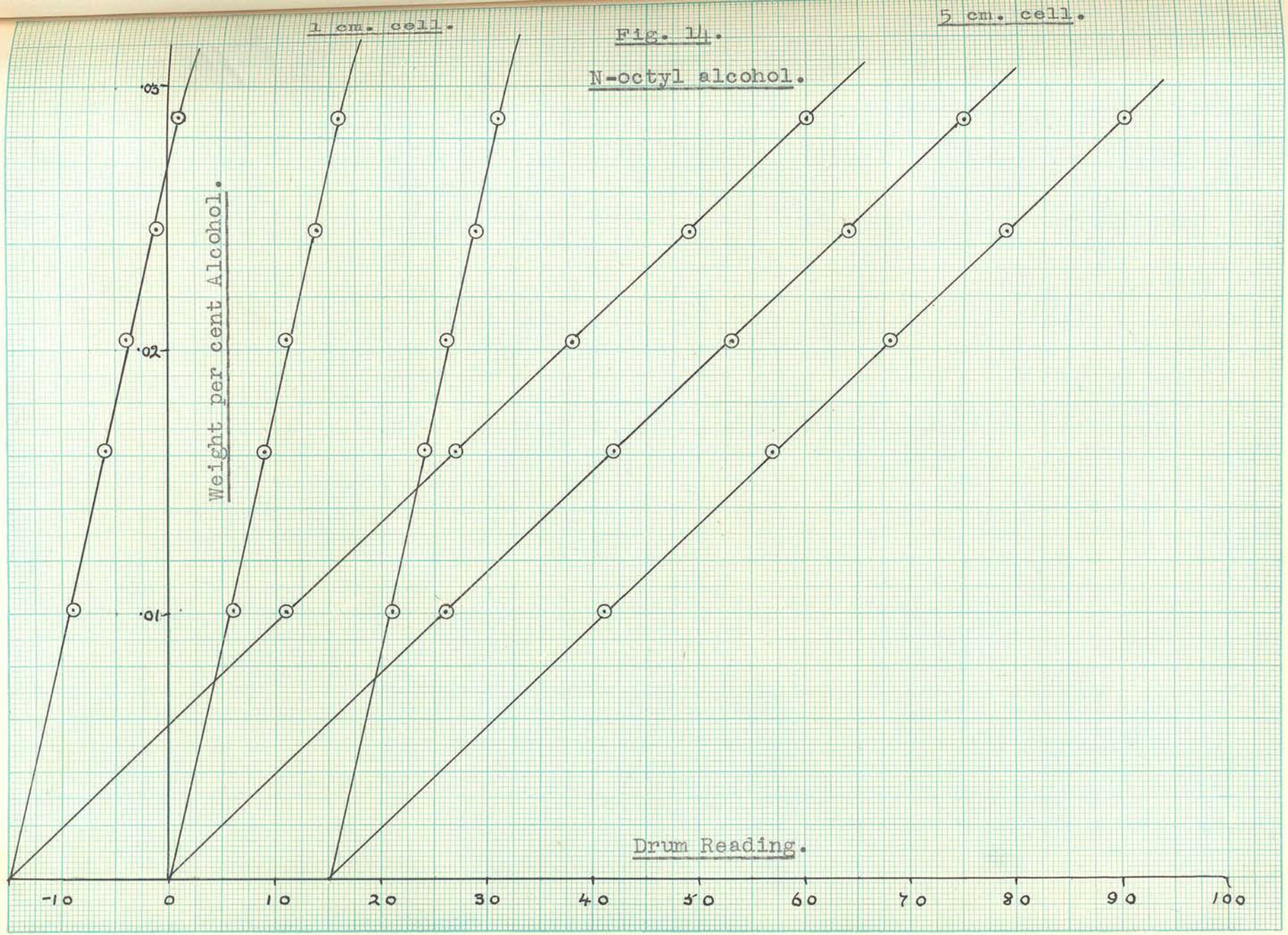
Solubility of water in n-amyl alcohol.

Attempts were made to determine the solubility of water in amyl alcohol since, from such a figure, the free energy difference of water in amyl alcohol solution could be derived in a manner similar to the above for the alcohols in aqueous solution.

Dilute solutions of water in amyl alcohol were made up by weight in order to calibrate the inter-:ferometer cells over a suitable range of composition using amyl alcohol as the standard liquid. These alcoholic solutions, however, seeped over the edges of the cells and caused considerable distortion of the fringes making it very difficult to obtain a drum reading. In addition, the readings finally obtained varied very little with change in composition of the solution used. This method was abandoned as being unsuitable.

The variation of viscosity with concentration was next considered as a possible means of obtaining the desired result. The dilute solutions of water in amyl alcohol were used to calibrate a viscosimeter but revealed the fact that the variation of viscosity with composition over the desired range was small, only about 2% between the pure alcohol and the saturated solution.

It was then decided to make use of the existing calibration of the interferometer cells at low concentrations. About ·5 gms. of the alcohol phase


1 cm. cell.
5 cm. cell.
Fig. 1/4.
N-octyl alcohol.
Weight per cent Alcohol.
·03
·02
·01
Drum Reading.
-10
0
10
20
30
40
50
60
70
80
90
100

was transferred to a weighed flask and its weight determined accurately. This was then diluted with water by a known amount, to come within the calibrat-:ion range of composition and a drum reading taken with each cell in comparison with water. The method of fixing the value of the composition of this solution was as previously described but, because of the large dilution required, the value of the solubility of water in amyl alcohol derived from this, was not very accurate.

The determination of the solubility of water in the other alcohols was not attempted. It is very desirable to have these data, but methods of a different nature will have to be worked out.

IV. EXPERIMENTAL DATA.

The calibrations of the interferometer cells for each of the four alcohols, are given in Table 7. The composition is given in weight per cent alcohol and, of the three drum readings given, the central figure is that for the apparent central fringe.

Table 7.

COMPOSITION.	DRUM READINGS. 1 cm. cell	5 cm. cell
N-amyl alcohol.		
0·0715	25, 40, 55.	142, 157, 172.
0·1048	44, 59, 74.	217, 232, 247.
0·1352	59, 74, 89.	280, 295, 310.
0·1635	74, 89, 104.	340, 355, 370.
0·3163	154, 169, 184.	685, 700, 715.
0·2500	120, 135, 150.	544, 559, 574.
N-hexyl alcohol.		
0·0310	3, 18, 33.	57, 72, 87.
0·0472	15, 30, 45.	101, 116, 131.
0·0634	23, 38, 53.	140, 155, 170.
0·0866	39, 54, 69.	196, 211, 226.
0·1064	47, 62, 77.	235, 250, 265.
0·1247	62, 77, 92.	291, 306, 321.
N-heptyl alcohol.		
0·00764	-11, 4, 19.	4, 19, 34.
0·01190	- 8, 7, 22.	13, 28, 43.
0·01963	- 3, 12, 27.	34, 49, 64.
0·02794	2, 17, 32.	54, 69, 84.
0·03166	5, 20, 35.	64, 79, 94.
0·03949	9, 24, 39.	82, 97, 112.
0·04741	14, 29, 44.	102, 117, 132.

(Continued) Table 7.

COMPOSITION.	DRUM READINGS. 1 cm. cell	5 cm. cell
N-octyl alcohol.		
0·01001	-9, 6, 21.	11, 26, 41.
0·01619	-6, 9, 24.	27, 42, 57.
0·02047	-4, 11, 26.	38, 53, 68.
0·02446	-1, 14, 29.	49, 64, 79.
0·02878	1, 16, 31.	60, 75, 90.

Table 8 gives the composition of the water phase for all four alcohols and also the approximate values of the concentration of alcohol in the alcohol phase of the amyl alcohol-water system. The compositions are expressed in weight per cent of alcohol.

Table 8.

ALCOHOL.	AMYL.		HEXYL.	HEPTYL.	OCTYL.
	Water phase.	Alcohol phase.			
Composition	2·209	92·0	0·636(7)	0·179(3)	0·0571(0)
	2·203	92·4	0·625(1)	0·183(6)	0·0606(4)
	2·207	93·0	0·621(8)	0·180(0)	0·0590(4)
	2·212		0·615(0)	0·181(8)	0·0586(8)
	2·211		0·610(9)	0·180(1)	0·0582(5)
			0·626(9)	0·178(7)	0·0579(7)
			0·634(1)	0·182(1)	
MEAN.	2·208	92·5	0·624(4)	0·180(7)	·0586

In Table 9 the solubility is expressed in weight per cent of alcohol W_a^s and also in mole fraction of alcohol N_a^s present in the water phase. The calculated values of the free energy difference are given under $(F_a^{o'} - F_a^o)$ in calories. The approximate figure of the mole fraction of alcohol present in the amyl alcohol layer is given under $N_a^{s'}$.

Table 9.

	W_a^s	N_a^s	$N_a^{s'}$	$F_a^{o'} - F_a^o$	Δ
N-amyl alcohol.	2·208	0·004596	·716	3190 cals.	844
N-hexyl alcohol.	0·6244	0·001107		4034 cals.	813
N-heptyl alcohol.	0·1807	0·0002808		4847 cals.	736
N-octyl alcohol.	0·0586	0·00008115		5583 cals.	

Table 10 shows the values of $F_a^{o'} - F_a^o$ for the whole series of normal alcohols up to C_8, and also of $F_w^{o'} - F_w$ for the cases in which the necessary data are available.

Table 10.

ALCOHOL.	f_a°.	$F_a^{\circ\prime}-F_a^{\circ}$.	Δ_a.	f_w°.	$F_w^{\circ\prime}-F_w^{\circ}$.	Δ_w.
Methyl.	1·507	240		1·62	290	
			500			260
Ethyl.	3·48	740		2·52	550	
			760			240
N-propyl.	12·5	1500		3·80	790	
			780			120
N-butyl.	46·5	2280		4·68	910	
			910			70
N-amyl.	218	3190		5·25	980	
			840			
N-hexyl.	903	4030				
			820			
N-heptyl.	3560	4850				
			730			
N-octyl.	12300	5580				

The activity coefficients of the alcohols above n-amyl, inclusive, have been calculated from $^1/N_a$, while the figures for ethyl, n-propyl and n-butyl alcohols have been slightly amended from those given by Thomson (loc. cit.) and quoted earlier in this thesis. The values of the free energy differences have been given in round numbers.

DISCUSSION.

As can be seen from the experimental data, each additional $-CH_2$ group in the hydrocarbon chain causes an approximately constant increment in the free energy difference $F_a^{o'} - F_a^{o}$ of 800 calories per gm. mol. Thus each additional $-CH_2$ group makes a contribution of 800 calories to the difference between the free energy of the alcohol molecule when surrounded by other alcohol molecules and by water molecules respectively. This indicates that the energy of interaction between a molecule and its surrounding molecules can be obtained by adding terms for the various groups in the molecule.

It is difficult to discuss such interactions except in terms of the surfaces of contact between the various groups. Langmuir has outlined a theory of solutions (Colloid Symposium Monograph, 3, 54, 1925) which is based upon the principle of "independ-:ent surface action", that is, it is postulated that the energy of interaction between a molecule and its surroundings can be obtained by summing the inter-:facial energies of the various surfaces of contact. After giving an outline of Langmuir's theory, we shall see how far the results, which have been obtained, are in accordance with it.

Consider a binary solution of two volatile liquids A and B, both molecules having composite surfaces. Let the components of molecule A be P and Q and of molecule B be R and S. Let the

fraction of the surface of the molecule A which is occupied by P be p and the fraction occupied by Q be q. Similarly, let the surface of the molecule B be occupied by a fraction r of R surface and a fraction s of S surface, so that:-

$$p + q = 1 \quad \text{and} \quad r + s = 1.$$

Let the molar fraction of A-molecules be A and of B-molecules B. Assuming random distribution of the molecules, that is, that there is no orientation or segregation of the molecules which surround any given molecule, the relative probabilities of any point on one molecule being in contact with an A-molecule or a B-molecule, will be proportional to the fractional surface areas of each kind in the solution.

The surface fractions of A and B in the solution are:-

$$\alpha = S_A^A / S_A^A + S_B^B \quad \text{and} \quad \beta = S_B^B / S_A^A + S_B^B$$

where α and β are the surface fractions and S_A and S_B are the surface areas of the A- and B-molecules respectively. Then

$$A + B = 1 \quad \text{and} \quad \alpha + \beta = 1$$

Assuming that the interfacial energy between two surfaces is independent of the nature of the rest of the molecule of which the surfaces are a part, the surface energy of a molecule of A in the binary solution, is found by summing the energies of the interfaces. These are PR, PS, PQ, QR and QS. The

interfaces between like surfaces are neglected since there is no surface energy in such a case.

Consider the interface PR. The area of molecule A which has a surface P is $S_A p$. Of this area a fraction β is in contact with B-molecules and of this again a fraction r is in contact with an R surface. The total area of this molecule which is a surface between P and R is therefore $S_A p\beta r$. If the interfacial energy between a P surface and an R surface is γ_{PR} ergs/cm^2, the energy at the interface PR is $S_A p\beta r \gamma_{PR}$. The other interfacial energies can be similarly obtained and the surface energy λ_1 of the molecule A in the binary solution is given by:-

$$\lambda_1 = S_A\left[2\alpha p q \gamma_{PQ} + \beta(p r \gamma_{PR} + p s \gamma_{PS} + q r \gamma_{QR} + q s \gamma_{QS})\right]$$

.....(16)

Let the molecule A be removed to the vapour phase leaving a cavity in the liquid. The surface energy of the molecule is now given by:-

$$\lambda_2 = S_A(p\gamma_P + q\gamma_Q)$$

.....(17)

and the surface energy of the cavity in the liquid by:-

$$\lambda_3 = S_A\left[\alpha(p\gamma_P + q\gamma_Q) + \beta(r\gamma_R + s\gamma_S)\right]$$

.....(18)

When the cavity is allowed to collapse the surface energy λ_3 disappears and new interfaces are formed which give rise to a new interfacial energy λ_4. The

surface of the cavity before collapse consists of the areas $S_A\alpha p$, $S_A\alpha q$, $S_B\beta r$ and $S_B\beta s$ of the four kinds of surface P, Q, R and S.

When the cavity collapses each of these areas forms contact with the others in proportion to their respective areas and we have the energy λ_4 appearing:-

$$\lambda_4 = S_A\left[\alpha^2 pq\gamma_{PQ} + \beta^2 rs\gamma_{RS} + \alpha\beta\left(pr\gamma_{PR} + ps\gamma_{PS} + qr\gamma_{QR} + qs\gamma_{QS}\right)\right]$$

.....(19)

The energy λ_{AV} necessary to transfer a molecule A from the binary solution to the vapour phase is then:-

$$\lambda_{AV} = \lambda_2 + \lambda_4 - \lambda_1 \qquad .....(20)$$

Substituting the values of λ_2, λ_4 and λ_1 and putting $\alpha = 1-\beta$ we have:-

$$\lambda_{AV} = S_A\left(p\gamma_P + q\gamma_Q - pq\gamma_{PQ} - \phi\beta^2\right) \qquad .....(21)$$

where the term ϕ is independent of the concentrations of the components in the solution, but is a function of the interfacial energies:-

$$\phi = \left(pr\gamma_{PR} + ps\gamma_{PS} + qr\gamma_{QR} + qs\gamma_{QS} - pq\gamma_{PQ} - rs\gamma_{RS}\right)$$

.....(22)

When the liquid consists of pure A, $\beta = 0$ so substituting this value into (21), we have the energy required to remove a molecule A from its pure liquid:-

$$\lambda'_{AV} = S_A\left(p\gamma_P + q\gamma_Q - pq\gamma_{PQ}\right) \qquad .....(23)$$

Thus equation (21) becomes:-

$$\lambda_{AV} = \lambda'_{AV} - S_A\phi\beta^2 \qquad .....(24)$$

The work required for the transfer of a molecule A from the pure liquid A to the given solution is thus:-

$$W_A = \lambda'_{AV} - \lambda_{AV} = \delta_A \phi \beta^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots(25)$$

and the activity coefficient of A in the solution, taking its value as unity in the pure liquid, is therefore given by:-

$$kT \log f_A = W_A = \delta_A \phi \beta^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots(26)$$

where k is the gas constant expressed per molecule, T the absolute temperature and f_A the activity coefficient.

In a very dilute solution of A in the solvent B, $\beta^2 = 1$ and we have:-

$$kT \log f_A^0 = \delta_A \phi \qquad \ldots\ldots\ldots\ldots\ldots\ldots(27)$$

Similarly, the work of transfer of the molecule B from pure liquid B to the given solution can be shown to be:-

$$W_B = \delta_B \phi \alpha^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots(28)$$

and its activity coefficient in the given solution shown by:-

$$kT \log f_B = W_B = \delta_B \phi \alpha^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots(29)$$

where f_B is the activity coefficient.

The activity coefficient of B in a very dilute solution in the solvent A is thus given by:-

$$kT \log f_B^0 = \delta_B \phi \qquad \ldots\ldots\ldots\ldots\ldots\ldots(30)$$

Smyth and Engel (J. Amer. Chem. Soc., 51, 2646, 1929) determined the partial vapour pressures of a number of binary solutions chosen so as to test these equations and found that, while the order of magnitude of the effects were in accordance with those postulated, quantitatively there were considerable deviations which they attributed to the effect of the electric dipoles in the molecules.

Application of equations to alcohol-water solutions.

In applying these equations to alcohol-water solutions we will suppose that A represents the alcohol molecule, P being the hydrocarbon chain and Q the hydroxyl group, and B the water molecule the surface of which we will consider to be homogeneous. Then the energy of interaction ϕ is, by equation (22)

$$\phi = p\gamma_{PB} + q\gamma_{QB} - pq\gamma_{PQ} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(31)$$

The activity coefficient of the alcohol at infinite dilution, from equation (27) is thus given by:-

$$kT \log f_A^\circ = s_A (p\gamma_{PB} + q\gamma_{QB} - pq\gamma_{PQ})$$

or

$$kT \log f_A^\circ = s_P\gamma_{PB} + s_Q\gamma_{QB} - ps_Q\gamma_{PQ} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(32)$$

where S_P and S_Q are the areas of the hydrocarbon chain and hydroxyl group respectively. We will consider first how this quantity varies as we pass up the series of alcohols.

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We can suppose that S_Q remains constant while S_P increases by a constant amount for each additional $-CH_2$ group. As the number of carbon atoms increases p approaches unity and the variation of the last term may, to a first approximation, be neglected. Then the variation of $kT \log f_A^\circ$ is:-

$$\Delta(kT \log f_A^\circ) = \Delta S_P \gamma_{PB} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (33)$$

where ΔS_P is the increment of area for each $-CH_2$ group.

The increment of $RT \log f_A^\circ$ or $(F_A^{o'} - F_A^\circ)$ for each additional carbon atom after the second, has been found to be about 800 calories per gm. mol. It will be interesting to see how this quantity compares with that calculated by (33) using for γ_{PB} the macroscopic interfacial energy between water and hydrocarbon. This may be taken as approximately 50 ergs per sq. cm. The increase in the area of the molecule for a $-CH_2$ group, regarding the molecules as cylinders with a cross sectional area of 20×10^{-16} sq. cm. and a distance of 1.5×10^{-8} cm. between each carbon atom and the next, is 22×10^{-16} sq. cm. We have then:-

$$\Delta(F_A^{o'} - F_A^\circ) = N \times \Delta(kT \log f_A^\circ) = N \Delta S_P \gamma_{PB}$$

where N is Avogadro's number thus expressing the equation (33) per gm. molecule instead of per molecule.

Therefore:-

$$\Delta(F_A^{o'} - F_A^\circ) = 6.06 \times 10^{23} \times 22 \times 10^{16} \times 50 / 4.18 \times 10^7$$
$$= 1594 \text{ calories.}$$

This is numerically about 100% higher than the observed value, but the agreement is probably as good as could be expected because the interfacial energy of cavities or surfaces of molecular dimensions must differ considerably from the macroscopic values.

The activity coefficient of water in alcohol at infinite dilution is given by:-

$$kT \log f_B^\circ = s_B (p\gamma_{PB} + q\gamma_{QB} - pq\gamma_{PQ}) \quad \ldots\ldots\ldots\ldots\ldots\ldots (34)$$

similar to equation (32). As we pass up the series of alcohols p gradually approaches unity and q diminishes towards zero. It is evident, therefore, that this quantity has a limiting value which is:-

$$kT \log f_B^\circ = s_B \gamma_{PB} \quad \ldots\ldots\ldots\ldots\ldots\ldots (35)$$

The data given in Tables 10 and 11 show that the activity coefficient of water at infinite dilution does appear to be approaching a limiting value.

Finally, by comparison of equations (32) and (34) we have:-

$$\log f_A^\circ / \log f_B^\circ = s_A / s_B \quad \ldots\ldots\ldots\ldots\ldots\ldots (36)$$

that is, the ratio of the activity coefficients of alcohol in water and water in alcohol, at infinite dilution should be equal to the ratio of their molecular areas. The following table gives the values of S_A/S_B determined in this way. This ratio increases by about 0·5 for each additional $-CH_2$

group, indicating that the increase of the surface caused by the latter is about half that of the water molecule. This is a reasonable figure, but the absolute magnitudes of S_A/S_B are less than might be expected from the molecular dimensions.

Table 11.

ALCOHOL.	$\log f_A^\circ$	$\log f_B^\circ$	S_A/S_B
Methyl.	0·18	0·21	0·9
Ethyl.	0·54	0·40	1·4
N-propyl.	1·10	0·58	1·9
N-butyl.	1·67	0·67	2·6
N-amyl.	2·34	0·72*	3·2

* Estimated from the solubility of water in the alcohol.

Variation of activity coefficients with concentration.

Langmuir's theory requires, according to equations (26) and (29), that:-

$$kT \log f_A^\circ = S_A \phi \beta^2$$

$$kT \log f_B^\circ = S_B \phi \alpha^2$$

where α and β are now the surface fractions of alcohol and water respectively. In addition to the data for methyl alcohol solutions given in this thesis, these equations can be tested on the data for ethyl alcohol obtained by Dobson and by Shaw and Butler (loc. cit.) and for n-propyl alcohol

obtained by Thomson (loc. cit.).

It has been found that the relative areas of the molecules which give the closest agreement with these equations are:- water 1, methyl alcohol 1·4, ethyl alcohol 1·8, n-propyl alcohol 2·2. Figs. 15 and 16 show the values of log f_A and log f_B for these substances plotted against β^2 and α^2 respectively. The necessary data are given in Table 12 where A and B are the mole fractions of alcohol and water given in round numbers, α^2 and β^2 the corresponding values of the surface fractions calculated from A and B and the ratio S_A/S_B, log f_A and log f_B the activity coefficients obtained from the smoothed curve of the activity coefficient plotted against mole fraction.

Fig. 15.

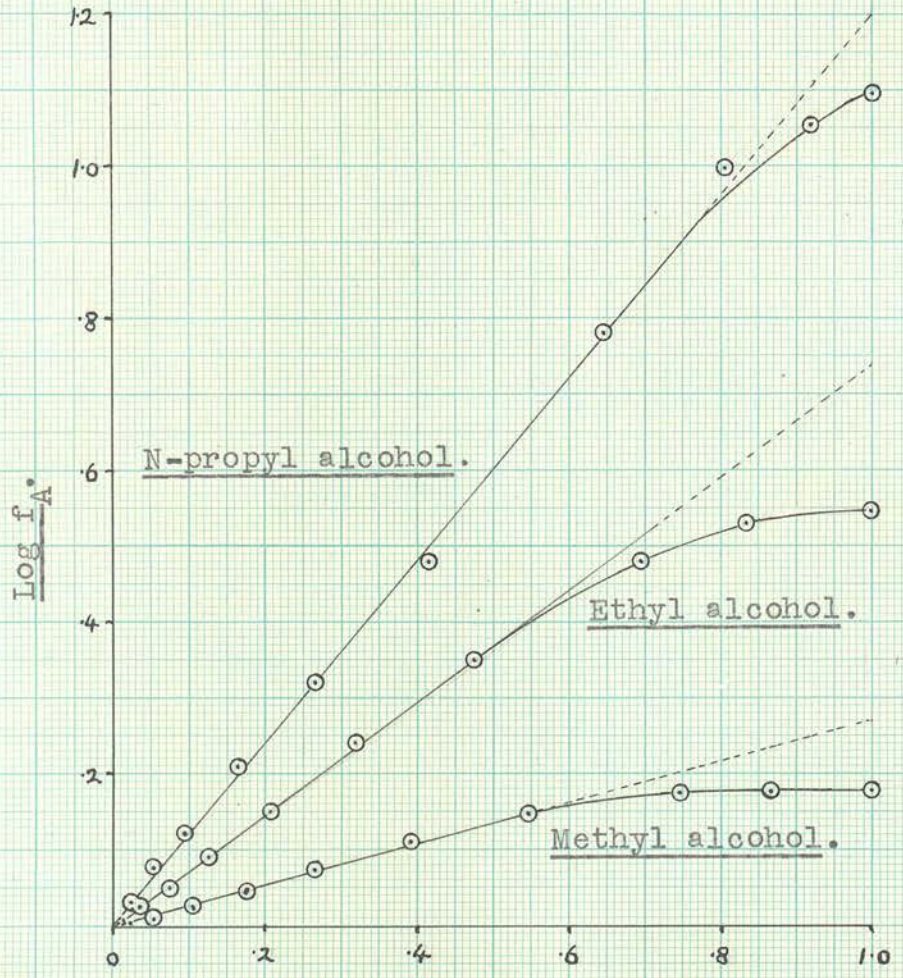

1·2
1·0
·8
·6
·4
·2
Log f_A.
N-propyl alcohol.
Ethyl alcohol.
Methyl alcohol.
0
·2
·4
·6
·8
1·0
β 2

Fig. 16.

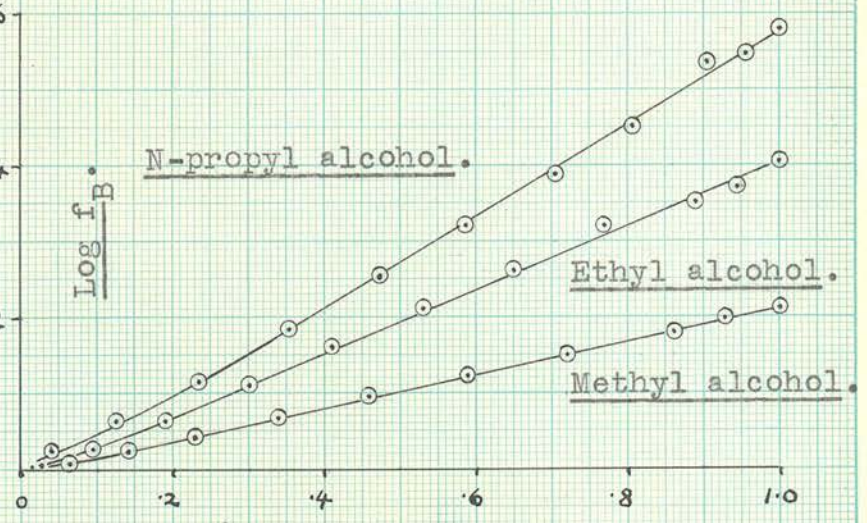

·6
·4
·2
Log f_B.
N-propyl alcohol.
Ethyl alcohol.
Methyl alcohol.
0
·2
·4
·6
·8
1·0
α 2

Table 12.

A	B	α^2	β^2	log f_A	log f_B
Methyl alcohol S_A/S_B = 1·4					
0·05	0·95		0·867	0·177	
0·1	0·9	0·018	0·749	0·173	0·002
0·2	0·8	0·067	0·549	0·148	0·009
0·3	0·7	0·141	0·391	0·110	0·023
0·4	0·6	0·233	0·267	0·072	0·042
0·5	0·5	0·340	0·174	0·043	0·067
0·6	0·4	0·458	0·104	0·021	0·096
0·7	0·3	0·587	0·055	0·009	0·123
0·8	0·2	0·720	0·023	0·004	0·150
0·9	0·1	0·858			0·180
0·95	0·05	0·929			0·198
Ethyl alcohol S_A/S_B = 1·8					
0·05	0·95		0·834	0·53	
0·1	0·9	0·029	0·694	0·48	0·004
0·2	0·8	0·096	0·476	0·35	0·023
0·3	0·7	0·189	0·319	0·24	0·061
0·4	0·6	0·297	0·207	0·15	0·107
0·5	0·5	0·413	0·127	0·09	0·161
0·6	0·4	0·533	0·073	0·05	0·209
0·7	0·3	0·653	0·037	0·025	0·260
0·8	0·2	0·771	0·015	0·004	0·318
0·9	0·1	0·887			0·352
0·95	0·05	0·945			0·373

(Continued) Table 12.

A	B	α^2	β^2	log f_A	log f_B
N-propyl alcohol S_A/S_B = 2·2					
0·02	0·98		0·920	1·550	
0·05	0·95		0·803	0·997	
0·1	0·9	0·038	0·646	0·78	0·026
0·2	0·8	0·126	0·416	0·48	0·061
0·3	0·7	0·235	0·265	0·32	0·117
0·4	0·6	0·354	0·164	0·21	0·182
0·5	0·5	0·473	0·098	0·12	0·253
0·6	0·4	0·588	0·054	0·073	0·320
0·7	0·3	0·701	0·027	0·030	0·389
0·8	0·2	0·806	0·010	0·008	0·450
0·9	0·1	0·906			0·534
0·95	0·05	0·954			0·548

The agreement is excellent for mole fractions of alcohol between 1·00 and 0·15 but in dilute solutions of the alcohols there is a marked deviation, the activity coefficients being less than is required by the equation. A similar deviation necessarily occurs in the same region of the water curves.

The following table shows the agreement between the observed activity coefficients of alcohol and those calculated by equation (26), using the value of $S_A\phi/kT$ obtained by extrapolating the linear parts of the curves in Fig. 15 to the axis $\beta^2 = 1$.

Table 13.

A	β^2	log f_A (calc.)	log f_A (obs.)
Methyl alcohol S_A/S_B = 1·4 and $S_A\phi/kT$ = 0·27			
0·1	0·749	0·202	0·173
0·2	0·549	0·148	0·148
0·3	0·391	0·106	0·110
0·4	0·267	0·072	0·072
0·5	0·174	0·047	0·043
0·6	0·104	0·028	0·021
0·7	0·055	0·015	0·009
0·8	0·023	0·006	0·004
Ethyl alcohol S_A/S_B = 1·8 and $S_A\phi/kT$ = 0·74			
0·1	0·694	0·514	0·48
0·2	0·476	0·352	0·35
0·3	0·319	0·236	0·24
0·4	0·207	0·153	0·15
0·5	0·127	0·094	0·09
0·6	0·073	0·054	0·05
0·7	0·037	0·027	0·025
0·8	0·015	0·011	0·004

(Continued) Table 13.

A	β^2	log f_A (calc.)	log f_A (obs.)
N-propyl alcohol	S_A/S_B = 2·2 and $S_A\phi/kT$ = 1·2		
0·1	0·646	0·775	0·78
0·2	0·416	0·499	0·48
0·3	0·265	0·318	0·32
0·4	0·164	0·197	0·21
0·5	0·098	0·117	0·12
0·6	0·054	0·065	0·073
0·7	0·027	0·032	0·030
0·8	0·010	0·012	0·008

Langmuir's theory thus accounts reasonably well not only for the differences between one alcohol and another, but also for the variation of the activity coefficient over the greater part of the range of concentration for any one alcohol. The divergences from the equations, which occur in dilute aqueous solutions, may be due to the failure of the assumption of an entirely random distribution and orientation of the molecules in these solutions. The effect of orientation, if it does occur, must be to reduce the interfacial energy.

It has been assumed that the water molecule has a homogeneous surface, but it may be that the inter-:facial energy between it and an alcohol molecule, is least for some particular orientation. The possibil-:ity of complete orientation of those molecules which

are in contact with alcohol is greatest in dilute solutions and, as the proportion of alcohol increases, it becomes increasingly difficult. In more concentrated solutions, it might be expected, as has been found to be the case, that the assumption of random distribution and orientation would work well.

SUMMARY.

(1) An air bubbling method has been used to determine the partial vapour pressures of aqueous solutions of methyl alcohol at 25°C.

(2) The activity coefficients of methyl alcohol and water at infinite dilution have been determined and the free energy difference calculated from these figures.

(3) The solubilities in water of the aliphatic alcohols from C_5 to C_8, inclusive, have been deter-:mined at 25°C and an approximate value obtained for the solubility of water in n-amyl alcohol, using an analytic method.

(4) The free energy differences of the higher alcohols have been calculated from their solubilities and the values so obtained confirm the hypothesis that the free energy difference increases by an approximate-:ly constant amount for each additional $-CH_2$ group. This increment is about 800 calories.

(5) Langmuir's theory of solutions has been applied to the solutions of the aliphatic alcohols in water. It is capable of accounting for the main features of the differences between one alcohol and another and for the variation of the activity coefficients of the lower alcohols with concentration except in solutions containing a large proportion of water. In these solutions marked deviations occur which may be due to orientation of the water round the alcohol molecules.

Part II.

The adsorption at the surface of aqueous solutions of methyl alcohol.

-----oOo-----

INTRODUCTION.

The variation, with concentration, of the surface excess of alcohol in aqueous solutions of ethyl and n-propyl alcohols at 25°C, has been accurately deter-:mined by Butler and Wightman (J. Chem. Soc., 2089, 1932) and Wightman (Thesis, Edinburgh University, 1932). The calculation of the surface excess requires accurate values of the partial vapour pressures of alcohol in the solutions in addition to reliable figures of the surface tensions of these solutions. The partial pressures of methyl alcohol in aqueous solutions have been accurately estimated in Part I of this thesis, but there do not appear to be any reliable values of the surface tensions of aqueous solutions of methyl alcohol at 25°C. Morgan and Neidle (J. Amer. Chem. Soc., 35, 1856, 1913) have determined the surface tensions of such solutions at 30°C using the drop weight method. It was, there-:fore, decided to extend the series of alcohols whose adsorptions have been studied, by determining the surface tensions of aqueous solutions of methyl alcohol at 25°C.

In a binary mixture, the excess of the solute in the region of the interface of a non-homogeneous system, or at the surface of a homogeneous system, is given by Gibb's equation:-

$$\Gamma_a = - d\gamma / dF$$

where Γ_a is the surface excess of the solute per unit area.

where $d\gamma$ is the change in surface or interfacial tension

dF is the change in partial free energy of the solute.

The variation of the partial free energy is given by:-

$$F = F_a^{\circ} + RT \log a$$

where a is the activity of the solute

F_a° is the free energy of the pure solute.

When the solute is volatile $a = p_a/p_a^{\circ}$, where p_a is the partial vapour pressure of the solute and p_a° is its vapour pressure in the pure state.

We have, therefore:-

$$dF = RT\, d\log p_a$$

Substituting the value of dF into Gibb's equation

$$\Gamma_a = -d\gamma / RT\, d\log p_a \qquad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

The surface excess or the adsorption is calculated from this equation.

EXPERIMENTAL.

I. Method of Experiment.

The capillary rise method was used to determine the surface tensions of the methyl alcohol-water mixtures.

If a capillary tube be made to dip vertically into a liquid which wets glass, the tendency for the liquid to spread over the surface causes the liquid to rise up inside the tube. This upward force is due to surface tension and is expressed as:-

$$2\pi r\gamma$$

where r is the radius of the tube and γ the surface tension of the liquid. As the liquid rises in the tube there is an increasing downward force acting on the liquid, the downward pull of gravity which is represented by:-

$$\pi r^2 hdg$$

where h is the height of the column of liquid above the surface, d is the density of the liquid and g is the acceleration due to gravity. When these two forces are in equilibrium the level of liquid in the tube will remain constant and the surface tension of the liquid will be:-

$$\gamma = rhdg/2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

For convenience in manipulation, the apparatus usually takes the form of a U-tube, one leg of which is a capillary, and the other a wide tube. When a

liquid is poured into the wide tube it rises to a higher level in the capillary tube and the difference in level between the two meniscuses represents h in equation (2). This type of apparatus was used.

Richards and Coombs (J. Amer. Chem. Soc., 37, 1656, 1915) have shown that the capillary rise determinations of surface tension are susceptible to quite serious errors most of which can be eliminat-:ed by using a suitable routine during the experiments. The chief source of error is, however, due to the use of a wide tube not large enough to give a plane surface from which to measure the rise in the capillary. Also, a correction has to be made for the capillary rise in the wide tube. The use of very wide tubes means that large quantities of liquids have to be used and there is difficulty in reading the level of the flat meniscus.

Rayleigh (Proc. Roy. Soc., 92A, 184, 1915) derived formulae to correct for the capillary rise in the wide tube, but their limited applicability limits the size of tube which may be used for accurate surface tension determinations. Sugden (J. Chem. Soc., 119, 1483, 1921) has shown how accurate values of surface tensions may be deduced from the difference in height of the meniscuses in any size of tube.

The correct value of the surface tension is given by:-

$$\gamma = hdg/2(1/b_1 - 1/b_2) \quad \ldots\ldots\ldots\ldots\ldots (3)$$

where b_1 and b_2 are the radii of curvature of the

meniscuses at their lowest points, in the narrow and wide tubes respectively. The values of b_1 and b_2 are obtained by using Sugden's tables in conjunction with a system of calculation described by him.

II. PREPARATION OF MATERIALS.

The methyl alcohol used during the experiments was prepared from the commercial alcohol by the method described in Part I (A) of this thesis. Its properties were:-

B.P. = 64·49°C (corrected) $D_4^{25^\circ}$ = ·78646 gm/c.c.

$n_D^{20^\circ}$ = 1·33063

III. APPARATUS AND PROCEDURE.

The capillary rise apparatus consisted of a U-tube, one limb of which formed the capillary, and the other, a wide tube, served to hold the bulk of solution. The capillary tube was made by drawing out, in the blow-pipe flame, capillary tubing of about 0·5 m.m. bore. After several attempts, a tube was obtained which gave a rise of about 11 cm. with pure water. The capillary was then fused on to a tube of about 3 cm. diameter. In the method of procedure, it was essential to be able to adjust the level of liquid in the capillary to the same point for every solution examined. To this end, the wide tube was fitted with a dropping funnel

from which the solutions could be added until the meniscus in the capillary was at a predetermined position. In addition, the wide tube was connected to a calcium chloride tube by rubber tubing so that, by blowing, the capillary surface could be thoroughly wetted with the solution to be examined.

The U-tube was clamped, partly immersed in the water, in a suitable position in a thermostat having plate glass sides and electrically heated and controlled to a temperature of 25 ± ·01°C. A bright source of illumination was placed behind the thermostat, into which the light diffused through a sheet of white paper. Sharp definition of the meniscuses was aided by the use of a black screen placed tangentially across them as advocated by Richards and Coombs (loc. cit.).

The measurements of the levels of the liquid in the apparatus were made by means of a cathetometer telescope reading to 0·005 cm.

The method of procedure adopted during the experiments was largely that outlined by Richards and Coombs. The tube was cleaned and grease removed by steeping it in chromic acid for a considerable time whilst being heated on a water bath. It was then washed thoroughly with distilled water and finally, immediately before use, with the solution under investigation.

The tube was then calibrated using pure water as the standard liquid. The water used throughout

the series of experiments was distilled water, redistilled with potassium permanganate to remove grease. A preliminary series of experiments was carried out to find a portion of the capillary tube which was of uniform diameter over a small range of length. When the level of water in the capillary was anywhere within this range, a reproducible value of the capillary rise was obtained. This point was marked on the tube. To calibrate the tube, water was run into it through the dropping funnel until, after blowing several times through the calcium chloride tube and removing the drop of liquid which appeared at the top of the capillary tube, the level of the liquid in the capillary was opposite the mark. The readings of the levels of the meniscuses were then taken and the process repeated until three concordant values of the difference were obtained for this sample of water. Two further samples were taken and the mean value of $\underline{h}$ for water estimated from these figures.

All the methyl alcohol solutions were made up by weight using grease free water. The experimental procedure for each solution was the same as for the calibration. Three samples were taken for each and the liquid level in the capillary was always adjusted to the mark so that the same portion of the tube was used during each determination. With the more concentrated solutions, it was found that the readings were not reproducible if they were taken at any appreciable time after adjusting the level.

An examination of the position of the meniscus after blowing the liquid up the capillary revealed the following. The meniscus gradually fell until its level became constant and remained so for some 2 minutes. Thereafter, it was seen to slowly rise until, after some time, it was considerably higher than the constant level. This phenomenon was not observed with pure water or with the more dilute solutions and was attributed to evaporation of the methyl alcohol from the surface of the solution in the capillary. The readings of the liquid levels were, therefore, taken immediately the meniscus stopped falling and no difficulty was experienced in reproducing the figures.

The whole range of solutions could not be investigated accurately by the use of the one tube because the difference in level h was not sufficiently great at higher alcohol concentrations. A second tube with a finer capillary was, therefore, used for the solutions containing more than 30% by weight of alcohol. This tube was cleaned and used in a manner similar to the other, but was calibrated with a solution whose surface tension had already been determined with the larger tube.

IV. EXPERIMENTAL DATA.

In Table I are given the results of the measurements of the surface tensions of methyl alcohol-water solutions over the range of 0-100% alcohol.

Table I/

Table I.

N_a	D	h		(approx.)	(corr.)
		cap. 1	cap. 2	γ	γ
0·00	0·9971	11·628		-	71·97
2·24	0·9911	10·303		63·39	63·42
2·74	0·9893	9·995		61·38	61·41
5·51	0·9816	9·167		55·85	55·88
7·73	0·9757	8·655		52·42	52·45
8·13	0·9748	8·527		51·60	51·63
8·95	0·9730	8·360		50·49	50·53
10·13	0·9717	8·137		49·08	49·12
11·87	0·9661	7·845		47·05	47·10
13·74	0·9618	7·556		45·11	45·16
15·68	0·9576	7·307		43·43	43·49
21·73	0·9442	6·698	11·459	39·26	39·34
25·93	0·9348		10·917	37·11	37·15
30·67	0·9243		10·449	35·12	35·16
47·19	0·8884		9·428	30·45	30·49
72·42	0·8377		8·500	25·89	25·93
100·00	0·7864		7·679	21·95	21·99

The concentration of alcohol in the solutions is given in mols per cent under N_a. The densities of the solutions are given under D at 25°C compared with water at 4°C and were obtained by interpolation from the values given in the Int. Crit. Tables, vol. 3, p. 115. The third column h gives the mean value of the capillary rise, in cms., obtained for three samples of each solution with the larger tube. Column four shows the figures obtained with the finer capillary; the solution of 21·73% of alcohol being the calibration solution for the smaller tube, has two corresponding values of h. The values of the surface tension, γ, given in the fifth column were calculated by simple proportion from h_s the capillary rise for the solution, h_w the rise for pure water, the densities of the solution and water, and γ = 71·97 dynes per cm. the surface tension of water at 25°C (Int. Crit. Tables, vol. 4, p. 447).

From equation (2) it is seen that γ_s the surface tension of the solution is given by:-

$$\gamma_s = h_s \times d_s / h_w \times d_w \times 71{\cdot}97 \text{ dynes per cm.}$$

where d_s is the density of the solution and d_w is the density of water.

The correct values of γ given in column six were calculated by equation (3) using Sugden's tables. The radius of the wide tube was obtained by measure-:ment and that of the capillary from the values of the surface tension and the observed capillary rise of water. These radii are used in the calculations

of γ correct.

The value of the surface tension of pure methyl alcohol obtained, 21·99 dynes per cm., is in agreement with 22·19 ± 0·2 dynes per cm., the figure interpolated from the values given in the Int. Crit. Tables, vol. 4, p. 448, at different temperatures and determined by both the capillary rise and drop weight methods.

The variation of surface tension with the mole percentage of alcohol in solution is shown in Fig. I.

Table 2 gives the calculated values of the adsorption for the solutions examined.

Table 2/

Fig. 1.

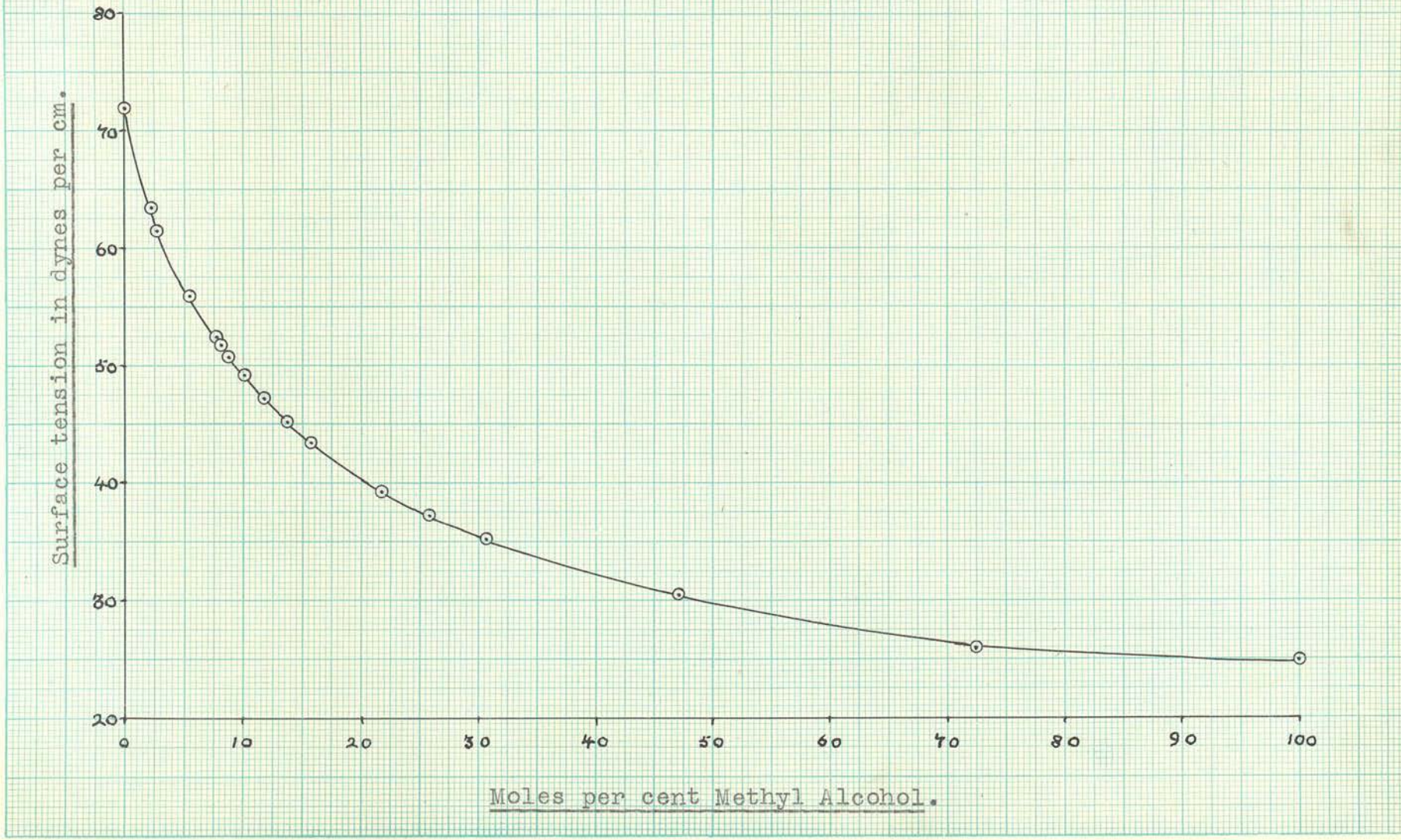
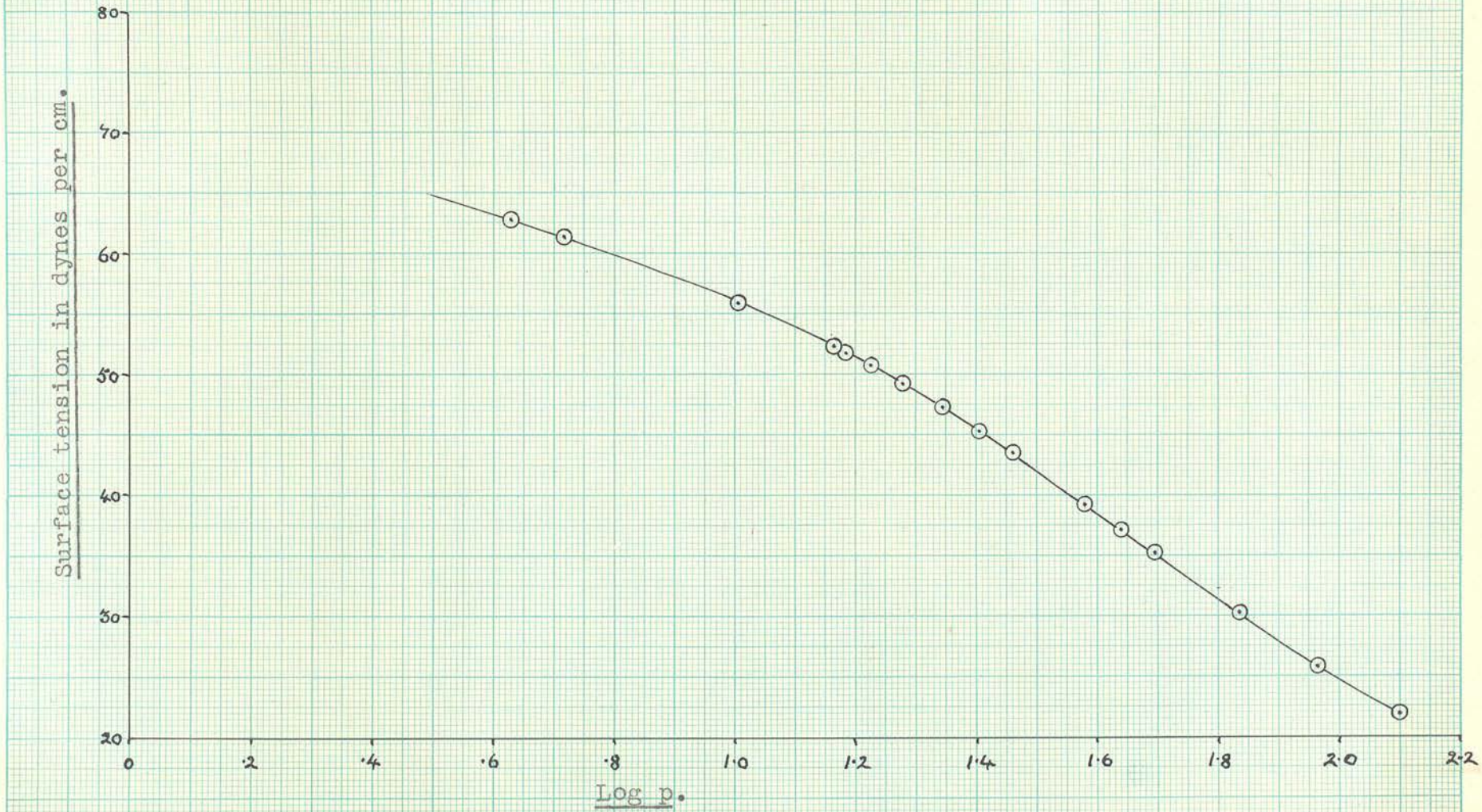

Surface tension in dynes per cm.
80
70
60
50
40
30
20
0
10
20
30
40
50
60
70
80
90
100
Moles per cent Methyl Alcohol.

Table 2.

N_a	Mean N_a	γ	$\Delta\gamma$	log p.	$-\Delta$log p.	$-\Delta\gamma/\Delta$log p.	$\Gamma/10^{13}$
2·24		62·68		0·630			
	2·49		1·27		0·087	14·6	15·5
2·74		61·41		0·717			
	3·93		5·53		0·303	18·3	19·4
5·51		55·88		1·020			
	6·62		3·60		0·146	24·7	26·2
7·73		52.28		1·166			
	7·93		0·65		0·021	31·0	32·9
8·13		51·63		1·187			
	8·54		1·10		0·041	26·8	28·5
8·95		50·53		1·228			
	9·54		1·41		0·052	27·1	28·8
10·13		49·12		1·280			
	11·00		2·02		0·067	30·1	32·0
11·87		47·10		1·347			
	12·81		1·86		0·060	31·0	32·9
13·74		45·24		1·407			
	14·71		1·75		0·055	31·8	33·8
15·68		43·49		1·462			
	18·71		4·15		0·119	34·9	37·1
21·73		39·34		1·581			
	23·83		2·19		0·061	35·9	38·1
25·93		37·15		1·642			
	28·30		1·99		0·056	35·5	37·7
30·67		35·16		1·698			
	38·93		4·67		0·130	35·9	38·1
47·19		30·49		1·828			
	59·81		4·56		0·141	32·3	34·3
72·42		25·93		1·969			
	86·21		3·94		0·134	29·4	31·2
100·00		21·99		2·103			

Fig. 2.


Surface tension in dynes per cm.
80
70
60
50
40
30
20
0
·2
·4
·6
·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
Log p.

The figures of the surface tension given in Table 2 are the smoothed values obtained from the curve of γ plotted against N_a. This involves an alteration from the values given in Table I in the case of solutions 2·24%, 7·73% and 13·74% alcohol. The second column shows the mean values of the composition between successive solutions.

The values of log p are obtained by interpolation from the curve of the activity coefficient plotted against composition as obtained in Part I of this thesis. The values so derived were considered to be more accurate than those interpolated from the curve of log p against N_a or from the vapour pressure curve. The variation of γ with log p is shown in Fig. 2.

Column four gives the increments in the surface tension and column six the corresponding decrements in log p for successive solutions.

The values of $-d\gamma/d\log p$ can be obtained by a graphical determination of the slopes of the curve shown in Fig. 2, but the process is not very accurate. They were, therefore, taken as being equal to $-\Delta\gamma/\Delta\log p$, the quotient of the increments of γ and log p for successive solutions, at the mean point of the corresponding interval. These values are given in column seven.

The value of the adsorption in molecules per sq. cm. is given by:-

$$\Gamma = -1/RT \times d\gamma/d\log p$$

where $1/RT$ is expressed as reciprocal ergs per molecule viz. -

$$1/2{\cdot}203 \times 1{\cdot}372 \times 10^{-16} \times 298 = 1{\cdot}062 \times 10^{13}$$

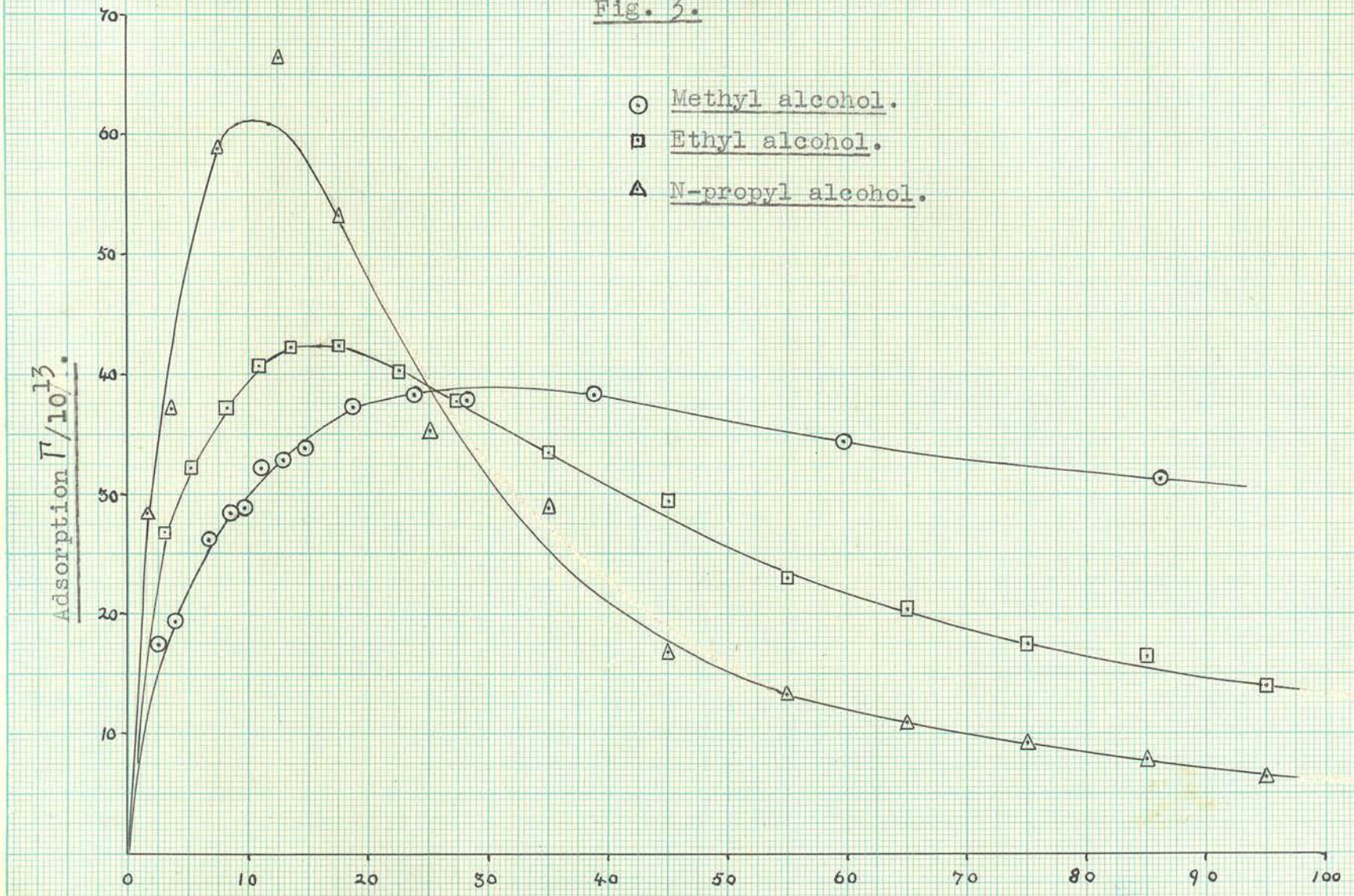
the gas constant R having value of $1{\cdot}372 \times 10^{-16}$ ergs per molecule. The values of $\Gamma/10^{13}$ corresponding to the mean values of N_a are listed in column eight.

Fig. 3 shows the variation of Γ with the mole percentage of alcohol in solution, obtained by plotting $\Gamma/10^{13}$ against the mean values of N_a, for methyl, ethyl and n-propyl alcohols. The data for the latter have been obtained by Wightman (loc. cit.). All three curves have the same form, that is, the adsorption rises to a maximum in dilute solutions and decreases again in more concentrated solutions. The curve for ethyl alcohol has been fully discussed by Butler and Wightman (loc. cit.).

In the case of methyl alcohol, the adsorption rises to a maximum value of $38{\cdot}3 \times 10^{13}$ molecules per sq. cm. at 30 moles per cent alcohol and thereafter falls to about 30×10^{13} molecules in very concentrated solutions. The corresponding figures for ethyl alcohol are $42{\cdot}5 \times 10^{13}$ at 15 moles per cent falling off to about 14×10^{13} and for n-propyl alcohol the maximum value is about 60×10^{13} molecules per sq. cm. at 10 moles per cent falling off to about $5{\cdot}5 \times 10^{13}$ molecules in very concentrated solutions.

It will be seen that, on passing up the series of alcohols, the maximum adsorption increases rapidly and is reached at lower concentrations with the higher members. Also, in more concentrated solutions of the

Fig. 3.


Methyl alcohol.
Ethyl alcohol.
N-propyl alcohol.
Adsorption $\Gamma/10^{13}$.
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
Moles per cent Methyl Alcohol.

latter, the adsorption falls off much more rapidly and is much less in very concentrated solutions.

SUMMARY.

(1) The surface tensions of water-methyl alcohol solutions have been determined at 25°C by the capillary rise method.

(2) The surface adsorptions have been calculated by the formula of Gibbs, using the vapour pressure measurements made in Part I of this thesis. The adsorption curve shows a maximum of $38{\cdot}3 \times 10^{13}$ molecules per sq. cm. at 30 moles per cent alcohol.

(3) This adsorption curve has been compared with the similar curves obtained for ethyl and n-propyl alcohols. The maximum adsorptions of these two alcohols are successively greater and occur at successively lower concentrations than for methyl alcohol. The adsorption in concentrated solutions is progressively less with increasing molecular weight.

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In conclusion I wish to acknowledge my indebted-:ness to the Carnegie Trust for a Scholarship during the tenure of which part of this work was done.

I also wish to express my thanks to Dr. J. A. V. Butler for his deep interest in the work, and for his many valuable suggestions.

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